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ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

V.—ON THE REACTION OF CERTAIN ALCOHOLS WITH PARA-DIAZOMETATOLUENESULPHONIC ACID.[1]

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Introduction.

Some time since it was desired to obtain a considerable quantity of metatoluenesulphonamide. Several methods of making the compound were on record, two of which were adapted to preparing it in quantity. In 1873 F. C. G. Müller[2] obtained it by reducing the barium salt of orthobrommetatoluenesulphonic acid by sodium amalgam and treating the product with phosphorus pentachloride and ammonia.

$$C_6H_3\begin{cases}CH_3\\Br(o)\\SO_3H(m)\end{cases} + H_2 = C_6H_3\begin{cases}CH_3\\SO_3H\end{cases} + HBr.$$

The following year v. Pechmann[3] obtained it by boiling paradiazometatoluenesulphonic acid with alcohol under a pressure of 200 mm. of mercury and treating the product with phosphorus pentachloride and ammonium hydrate.

$$C_6H_3\begin{cases}CH_3\\SO_3(m)\\N_2(p)\end{cases} + C_2H_5OH = C_6H_3\begin{cases}CH_3\\SO_3H\end{cases} + C_2H_4O + N_2.$$

[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1890.

[2] Ann. Chem. (Liebig), **173**, 295. [3] *Ibid.* **269**, 47.

It was observed, however, that the products obtained by the different processes were not identical. The difference lay principally in the melting-points of the amides, and in the solubility and water of crystallization of the salts of the corresponding sulphonic acids. Professor Remsen suggested to me that probably the discrepancies were due, in part at least, to the fact that the reaction did not take place wholly as v. Pechmann supposed, that there was formed also a certain amount of the ethoxy amide, which remained mixed with the metatoluenesulphonamide as an impurity. The reaction in this case would be

$$C_6H_3\begin{cases}CH_3\\SO_3\\N_2\end{cases} + C_2H_5OH = C_6H_3\begin{cases}CH_3\\SO_3H\\O.C_2H_5\end{cases} + N_2.$$

It was determined to test this hypothesis by a careful study of the action of alcohol on the diazo compound in question.

Preparation of Paratoluidinemetasulphonic Acid.

The paratoluidinemetasulphonic acid was made from paratoluidine according to the method of v. Pechmann.[1] To 100 grams of paratoluidine were added 200 grams of fuming sulphuric acid. Thereupon the mass heated, turned dark, and gave off fumes of sulphur dioxide. (It was found afterward that the yield was somewhat better if the paratoluidine was added gradually to the fuming sulphuric acid, with frequent stirring, thus preventing the temperature from rising too high.) The mixture was then kept at a temperature of 180° for about an hour. The heating should be stopped and the mass allowed to cool as soon as the odor of the sulphur dioxide fumes given off becomes marked. v. Pechmann's work has shown that if the heating is continued beyond this point, the comparative yield of paratoluidineorthosulphonic acid and of the disulphonic acid is much increased. After cooling, the material was poured into twice its volume of water; the mixed sulphonic acids crystallized on standing, giving a dark gray, semi-liquid, pasty mass; the liquid was drained off from this mass, as completely as possible, with a filter-pump and afterward by heavy pressure between the plates of a screw-press. The liquid thus obtained was very dark, almost black. On standing for two or three weeks there crystallized out from it a considerable quantity

[1] Ann. Chem. (Liebig) **173**, 195.

of long, thin plates apparently belonging to the triclinic system. These were purified by boiling with animal charcoal and by recrystallization. By this treatment they were obtained in a pure white condition, but were not examined further. In all probability they were crystals of the paratoluidinedisulphonic acid mentioned by v. Pechmann. The dark mass that remained after pressing the liquid out consisted principally of the meta- and orthosulphonic acids of toluidine. The remaining sulphuric acid was precipitated by an excess of barium hydroxide solution. The solution was then boiled briskly for some time to drive off any toluidine that might have remained unacted upon by the sulphuric acid. (As a rule, this was found unnecessary, but occasionally there remained quite an excess of unchanged toluidine.) The excess of barium was then precipitated as accurately as possible with sulphuric acid, the barium sulphate filtered off and the filtrate evaporated to crystallization. It was found that considerable quantities of the sulphonic acids were precipitated with the barium sulphate. It was therefore necessary to boil the precipitate several times with water, filter, and add this wash-water to the original filtrate in order to avoid serious loss of material. This is especially true when the solution is too concentrated. It is best to work with a large amount of water—say 8 to 10 liters for every 100 grams of the original toluidine. The solution, freed from barium and sulphuric acid—(a slight excess of sulphuric acid does no harm)—was evaporated until it began to crystallize, and then allowed to cool. On cooling, long, beautiful, sulphur-yellow needles of the meta acid crystallized out, seeming to fill the whole dish. The appearance is very deceptive, as the crystals shrink to a small bulk when filtered. They were filtered off and the mother-liquor evaporated nearly to dryness, and allowed to crystallize. A considerable quantity of the rhombohedral crystals of the ortho acid were obtained from the mother-liquor, some also from the first crystallization of the meta acid. The two acids may be separated either by the difference in the solubility of the lead salts or of the potassium salts, or by crystallizing the acids themselves from dilute alcohol.[1] The latter method was found more convenient and satisfactory, involving less loss of material.

If the needles of the meta acid are small (which result may be obtained by crystallizing rapidly with stirring), an almost com-

[1] Ann. Chem. (Liebig) **173**, 197; This Journal **8**, 274.

plete separation may be secured through the difference in the specific gravity of the two acids. The mixed acids were shaken up with a considerable quantity of dilute alcohol (say fifty per cent.), and, after partial settling, the light needles of the meta acid were poured off. By repeated shaking and settling and pouring back and forth (*i. e.*, by a sort of fractional decantation), the two acids may be obtained in a nearly pure condition. The separation is completed by a single crystallization from dilute alcohol in which the ortho acid is but very slightly soluble. The meta acid still retains a yellow color which it is difficult to remove. It may be obtained, however, in a pure white condition by repeated boiling with animal charcoal and by recrystallization.

Preparation of Paradiazometatoluenesulphonic Acid.

v. Pechmann[1] recommends diazotizing the meta acid by suspending either in alcohol or water and treating with nitrous acid. Later it was shown, however, that on account of the solubility of the diazo compound in water it is preferable to use alcohol.

Notwithstanding this, water was used as the medium in the first experiments tried. It was kept cool and a rapid stream of nitrous fumes passed through it. The reaction took place very rapidly. Some twenty grams of the acid were diazotized in less than ten minutes, the product being of a very faint pink tinge, nearly white. The yield, however, was very poor—less than fifty per cent. of the theoretical. A large proportion of the diazo compound remained in solution in the water, from which it could not easily be separated.

In all subsequent experiments ninety-two per cent. of alcohol was used (say 250 cc. to 25 grams of the acid), and was found to work very satisfactorily. The alcohol in which the finely pulverized acid was suspended was placed in an Erlenmeyer flask. On passing the nitrous fumes through it it gradually becomes hot, turning yellow, and finally a bright yellowish red. The yellow acid then changes rapidly over to the pink or pinkish white grains of the diazo compound. The whole process requires about thirty minutes. While the alcohol remains cold, little or no action takes place. By the action of the nitrous fumes the material is heated in ten or fifteen minutes, but time is saved by heating the alcohol to 26°–30° before beginning the operation. The temperature

[1] Ann. Chem. (Liebig) **173**, 201.

should not be allowed to rise above 40°, otherwise there is danger of considerable decomposition. The temperature may easily be regulated when there is danger of too great heat, by placing the flask in a dish of cold water. The higher the temperature at which the action takes place the darker is the pink color of the resulting diazo compound. By careful treatment, especially if absolute alcohol be used, the product may be obtained in a very nearly pure white condition. The action is hastened by continual shaking. When the action is complete the diazo compound is filtered by means of a filter-pump, washed with alcohol and then with a little ether. The yield is very good—eighty-five to ninety-five per cent. of the theoretical. 50–100 grams of the acid may conveniently be diazotized at one time. The diazo compound, if perfectly dry and kept in the dark, remains unchanged for a long time; if left in a moist condition it rapidly turns yellow. Even the dry compound gradually decomposes when exposed to the light, though it may be kept for several days without undergoing any change.

It is interesting to note in passing that the metasulphonic acid of paratoluidine is more easily diazotized than the corresponding ortho acid, both in water and in alcohol. In several of the diazotizing experiments that were tried, the meta acid used contained a small amount of ortho acid as an impurity. In these cases there remained invariably a residue of the ortho acid after all the meta acid had passed over into the diazo compound. The same fact was observed when water was used as the medium in which the acid was suspended. To test the point more carefully two grams of the acid were ground up together, and ninety-two per cent. of alcohol added to the mixture; nitrous fumes were passed through it for about thirty minutes; there then remained a considerable residue of the unchanged ortho acid, while all of the meta acid had been converted into the diazo compound. The mixture was shaken rapidly during the whole of the diazotizing process, to prevent any separation of the two acids by the difference in their specific gravity. The experiments show that the meta acid is more easily diazotized than the ortho acid.

Action of Ethyl Alcohol on Paradiazometatoluenesulphonic Acid.

Twenty-five grams of the diazo compound were boiled with 400 cc. of alcohol (98-per cent.) under a pressure of 195–210 mm.

of mercury in the apparatus used by Remsen and Palmer,[1] and by Remsen and Dashiell.[2] At first there appeared to be no change, but soon the alcohol began to turn yellow, then gradually changed through orange color to a dark red. The suspended diazo compound meanwhile had been dissolved, leaving a clear red solution. During the boiling there was a slight odor of aldehyde. The reaction is completed when the diazo compound is entirely dissolved. This took place in about twenty-five minutes, but the boiling was continued for some time.

In a subsequent experiment 20 grams of the diazo compound were boiled with 300 cc. of alcohol (98-per cent.) under 400 mm. pressure. The solution seemed to be complete in ten minutes, but the boiling was continued for half an hour. In this experiment also there was only a slight odor of aldehyde.

The dark red liquid obtained in this way was strongly acid in its reaction. It was heated to boiling on a water-bath, and neutralized, as nearly as possible, with dry sodium carbonate. The neutral or slightly alkaline solution was then evaporated to dryness on a water-bath, and finally powdered and dried in an air-bath. It was found in the experiments that if any water was mixed with the solution, the process of drying was an exceedingly tedious one. On evaporating it formed a dark brown, gummy mass from which it was very difficult to drive off all the water. If, however, all the water was carefully excluded, the strong alcoholic solution evaporated and dried rapidly. The dried sodium salt was finely pulverized and treated with somewhat more than an equal weight of phosphorus pentachloride. After the reaction there remained a red oil. This was washed in a large amount of cold water and treated with concentrated ammonia solution, in the usual way, to form the amide. On adding ammonia the substance became hot, assumed a bright yellow color, and gradually became solid. After the completion of the reaction the ammonia was evaporated on a water-bath, and there remained a dark red, gummy, semi-crystallized mass. This was boiled repeatedly with a large amount of water until nearly all was dissolved. There remained undissolved a small amount of a dark brown, tarry substance. The water, with the substance in solution, was filtered and allowed to cool, when there crystallized out a considerable quantity of yellowish needles, mixed with more or less gummy

[1] This Journal **8**, 243. [2] *Ibid.* **15**, 105.

material. This was boiled with animal charcoal and recrystallized five times, and thus the substance was obtained in the form of pure white needles with a constant melting-point 138°–139°. (The metatoluenesulphonamide, obtained by v. Pechmann, crystallized in rhombohedral scales and melted "somewhat below 100°.") The compound is moderately soluble in boiling water, but very slightly so in cold water. It dissolves easily in cold alcohol, ether, and acetone. Hot benzene dissolves it readily. Analysis showed its composition to be $C_9H_{13}O_2NS$. The results obtained were as follows:

.20251 gram of the substance gave .2205 gram barium sulphate = 14.97 per cent. S. The determination was made by Liebig's method. (Two determinations were made by Pearson's method which gave an average 0.51 per cent. too low. Other determinations, in this laboratory, by Pearson's method, of certain difficultly decomposable sulphonamides have given similar results.)

.25100 gram of the substance gave ammonia equivalent to 10.86 cc. of a standard ammonia solution containing 1.4672 grams of nitrogen to the liter.

.24822 gram of the substance gave .45478 gram of carbon dioxide and .1341 gram of water.

For $C_9H_{13}O_2NS$:

		Theory.	Found.
C_9	108	50.23	49.96
H_{13}	13	6.05	6.00
O_2	48	22.33	...
N	14	6.51	6.35
S	32	14.88	14.97
	215	100.00	

The compound formed was undoubtedly paraethoxymetatoluenesulphonamide, $C_6H_3\begin{cases}CH_3\\SO_2NH_2(m)\\O.C_2H_5(p)\end{cases}$.

This is one of some thirty known cases in which a diazo compound boiled with alcohol gives a substance in which the diazo group is replaced by the ethoxy group instead of by hydrogen. The yield of the ethoxy compound was poor; of the purified substance there was obtained only a little over nine per cent. of the theoretical. The actual yield was of course considerably larger,

there being more or less loss of material in the repeated crystallizations necessary for purification. The small yield of the ethoxy compound suggests, of course, that most of the diazo compound was acted upon in the regular way, giving the reaction

$$C_6H_3\begin{cases}CH_3\\SO_3(m)\\N_2(p)\end{cases} + C_2H_5OH = C_6H_4\begin{cases}CH_3\\SO_3H(m)\end{cases} + C_2H_4O + N_2.$$

But the absence of any strong odor of aldehyde during the reaction renders it improbable that the metatoluenesulphonic acid was produced to any considerable extent. To determine this point accurately, all the mother-liquors of the different crystallizations of the ethoxy compound were worked over with great care. There was obtained, in this way, a small quantity of a mixture made up evidently of the small rhombic scales of metatoluenesulphonamide, together with more or less of the paraethoxy derivative of the same. With the small quantity at hand it was found impossible, by repeated crystallizations, to separate the two compounds completely. Possibly with larger quantities this might be effected more easily. The different crystallizations made in the effort to purify the metasulphonamide gave various mixtures melting between the points 98° and 108°. Usually the mixtures had no sharp melting-point, but melted through several degrees. A few mixtures were obtained, however, that seemed to have a fairly definite melting-point. One, for example, melted quite sharply at 105°, and recrystallization in a small amount of water in a test-tube produced little change. By recrystallizing in a large amount of water, however, and filtering off the first of the material that crystallized out, a small quantity of the ethoxy derivative was obtained in a nearly pure condition.[1]

The experiments prove beyond question that the two amides crystallize together in mixtures that are exceedingly difficult to separate and which might easily be mistaken for approximately pure substances. It is highly probable that this fact furnishes an explanation of the hitherto unexplained discrepancies between the metatoluenesulphonic acid made from the diazo compound and that made according to Müller. The sulphonamide which v. Pechmann obtained from the diazo compound had no definite melting-

[1] Nevile and Winther (Ber. d. chem. Ges. **13**, 1947, and Journ. Chem. Soc. **37**, 625) give 106.5°–107.5° as the melting-point of the amide obtained by them in small quantity.

point. He speaks of it as melting "somewhat below 100°." It was probably a mixture of the two amides.

Preparation of Paraethoxymetasulphaminebenzoic Acid.

Five grams of the ethoxy amide were placed in a flask, together with 190 cc. of water and 1.8 grams of caustic potash, and heated in a water-bath until the amide was entirely dissolved. There was then added a hot solution of 8 grams of potassium permanganate in 190 cc. of water. The whole was heated in a water-bath until the color disappeared, leaving a yellow liquid above the dark brown deposit of manganese hydroxide. This, on cooling, deposited a considerable quantity of the unchanged amide. More potassium permanganate was therefore added, and the heating was continued until decolorization took place. The manganese hydroxide was then filtered off and the liquid allowed to cool. After filtering to remove the small amount of unchanged amide which crystallized out, the solution was acidified with hydrochloric acid. This gave a copious precipitate of fine white needles. In order to remove the small amount of the original amide which was contained in the precipitate, it was first dissolved in hot dilute sodium carbonate, and the solution evaporated to dryness. The dried mass was treated with a small amount of cold water, the solution filtered, and the filtrate acidified. The pure white needles obtained in this way were recrystallized from water. They were almost insoluble in cold and difficultly soluble in boiling water. The solution gave a strongly acid reaction. Two and a half grams of the substance were obtained in long, beautiful needles which seemed to be perfectly pure. It melted at 220°–230°, with gradual decomposition, as shown by the brown color which deepened as the temperature rose. For fear that this indicated impurity, the whole was converted into the barium salt by neutralizing the boiling solution with pure barium carbonate. The filtrate was evaporated to dryness, and thus the barium salt was obtained in the form of fine, pure white needles, only moderately soluble in cold water, but very slightly soluble in hot absolute alcohol. The salt was boiled in absolute alcohol to remove the last traces of the original amide, and then recrystallized once from water. After determining the water and barium in this salt, it was dissolved and the acid again precipitated with hydrochloric

acid. It was then washed thoroughly and recrystallized once from water. A determination was made of the nitrogen in the acid so obtained. The analyses gave for the barium salt the formula $C_{18}H_{20}O_{10}N_2S_2Ba.2H_2O$, and for the acid the formula $C_9H_{11}O_5NS$.

.1661 gram of the barium salt gave .00899 gram of water (at 210°) and .0588 gram of barium sulphate. This gives for water 5.41 per cent.—theory 5.45 per cent.—and for barium 20.80 per cent.—theory 20.70 per cent.

	For $C_{18}H_{20}O_{10}N_2S_2Ba.2H_2O$. Theory.	Found.
H_2O	5.45	5.41
Ba	20.70	20.80

.2099 gram of the acid gave NH_3, equivalent to 8.047 cc. of a standard ammonia solution containing 1.4672 grams of nitrogen to the liter. This gives for nitrogen 5.63 per cent.; theory, 5.71. The acid contained no water of crystallization.

These analyses prove the essential purity of the acid, but the melting-point was still by no means sharp. The material melted mostly at 230°–231°. It showed signs of melting, however, at 225°. The molten substance had a brown color, indicating partial decomposition.

By fusion with potassium hydroxide this acid passes over easily into protocatechuic acid, as was to be expected.

Action of Methyl Alcohol on Paradiazometatoluenesulphonic Acid.

The study of the action of ethyl alcohol on paradiazometatoluenesulphonic acid naturally suggested the question whether methyl alcohol would act in the same way. The question was tested, and the results obtained were, in general, analogous to those obtained in the case of ethyl alcohol. The reaction was found to work more perfectly, however, with the methyl alcohol.

18.5 grams of the diazo compound were boiled with methyl alcohol for fifty minutes, under a pressure of 450 mm. The temperature of the alcohol boiling at this pressure was 78°. Under ordinary pressure it distilled over between the limits 65°–66°. As the diazo compound dissolved, the color turned clear dark red, resembling in appearance the corresponding liquid obtained with ethyl alcohol. The solution was heated nearly to boiling in an

evaporating-dish, and then neutralized with dry sodium carbonate. The sodium salt so formed was difficultly soluble in methyl alcohol. It was precipitated so copiously that the whole became semi-solid, even before neutralization was complete. The salt was then partially dried on the water-bath, and finally pulverized, and the drying completed in an air-bath at 110°. If all water be carefully excluded, the whole process of drying requires less than an hour. The salt so obtained was a light brown, nearly white powder.

Preparation of Paramethoxymetatoluenesulphonic Chloride.

Treated with an equal weight of phosphorus pentachloride and washed with cold water, the sodium salt gave a dark brown oil, much lighter colored, however, than the corresponding ethyl compound. This oil solidified, on cooling, to a semi-crystalline mass. By several recrystallizations from commercial benzene it yields a pure crystalline substance of a faint yellow, or cream, color. Long boiling with animal charcoal and repeated crystallizations failed to remove this color. It melted sharply at 84°. It is easily soluble in cold ether and acetone. In boiling benzene it dissolves readily, and is deposited again, almost completely, as the solution cools. Benzene, therefore, forms the best solvent from which to recrystallize it. In boiling water it dissolves slowly, with decomposition. When crystallized rapidly from a concentrated solution it comes down in the form of fine needles; by spontaneous evaporation from benzene, in beautiful aggregates of large orthorhombic plates. By spontaneous evaporation of a long, narrow column of the ether solution, thicker crystals were obtained, showing a greater variety of faces. The following planes were observed: basal plane, prism, macropinacoid, brachypinacoid, macrodome, brachydome, and perhaps the pyramid. The crystals were shown to belong to the orthorhombic system by the interference figures and the parallel extinction.

A chlorine determination indicated the following formula: $C_8H_9O_3SCl$.

.12349 gram of the chloride gave .0799 gram of silver chloride. This gives chlorine 16.01 per cent.—theory, 16.06 per cent. This analysis was confirmed, as will be described later, by analysis of the corresponding amide and of various salts of the corresponding acid.

The best yield that was obtained was a little less than fifty per cent. of theoretical.

On working over the benzene mother-liquors a small amount of a red oil was obtained, insoluble in cold water, soluble with decomposition in boiling water, forming a solution with which silver nitrate gives a copious precipitate of silver chloride. This oil was not examined with care, but was, in all probability, the metasulphon chloride of toluene. The corresponding amide was formed by treating the oil with concentrated ammonia, but the quantity was so small that it was impossible to identify it clearly. It is certain that this action takes place, to some extent, in connection with the methoxy reaction, as will be shown later in connection with the amide.

Preparation of Paramethoxymetatoluenesulphonic Acid.

In order to obtain the acid corresponding to the methoxysulphonic chloride, ten grams of the purified chloride were boiled with about one liter of distilled water for an hour and a half (a balloon flask with an inverted condenser being used to prevent loss). At the end of this time the solution was nearly complete. There remained only a slight impurity suspended in the fluid. The solution, when filtered, was colorless. On evaporating it turned somewhat brown and yielded long, yellowish needles, quite easily soluble in water. These were dissolved, boiled with animal charcoal and filtered. In this way a perfectly colorless solution was obtained, but on evaporation it again turned brown, yielding a crystalline substance which still had a yellowish color. The melting-point also indicated that the substance was impure. Its solution contained a small amount of sulphuric acid, which must have come from the decomposition of the acid. It was found, however, that this acid, when dissolved in water and purified with animal charcoal, yielded pure salts with the carbonates of barium and lead.

In order to obtain a pure specimen of the acid, two or three grams of the pure lead salt were made (see below). This was dissolved in water and the lead precipitated from the solution by hydrogen sulphide. The perfectly colorless solution left after filtering off the lead sulphide, was evaporated over a water-bath. This also turned dark as it approached concentration and gave a brown product. Another portion of the lead salt was then prepared and precipitated by hydrogen sulphide, and the colorless

solution thus obtained was evaporated on a water-bath until it began to have a faint yellowish tinge. It was then allowed to evaporate spontaneously in a vacuum. After four or five days the evaporation was complete and the acid was obtained in a nearly pure condition. It still had a yellowish brown color, however. Undoubtedly, the perfectly pure acid is white. The acid melted at 92°–95°. It evidently decomposes somewhat on evaporation over a water-bath. It was not analyzed, as its composition was sufficiently plain from the mode of formation and the analysis of its salts.

Barium Salt.—The barium salt which crystallizes in needles is exceedingly soluble in water; slightly, if at all, soluble in cold alcohol or ether. It is moderately soluble in boiling alcohol. Barium determinations gave the following result:

I. .27888 gram of the salt gave .12070 gram of barium sulphate.

II. .29986 gram of the salt gave .12947 gram of barium sulphate.

For $Ba\left(C_6H_3\begin{matrix}CH_3\\SO_3\\O.CH_3\end{matrix}\right)_2$.

	Theory.	Found.
Ba	25.39	25.43–25.37

The specimen analyzed was obtained by evaporating the solution to dryness on a water-bath. So prepared, it contained no water of crystallization.

Calcium Salt.—This salt crystallizes in white or slightly yellowish needles. It is exceedingly soluble in water, difficultly soluble in cold alcohol. It dissolves much more easily in boiling alcohol, but, like the barium salt, it does not crystallize easily from this medium except by spontaneous evaporation. There seemed to be a strong tendency to form a supersaturated solution from which the salt would not separate except by evaporation. It is strongly hygroscopic. After drying on a water-bath it absorbs water rapidly, but takes up no definite amount, as was shown by several determinations. It cannot be dried in a desiccator. The salt was dried at 170°, and then three determinations of the calcium were made, which gave the following results:

.21276 gram of the salt gave .06763 gram calcium sulphate.

.17400 gram of the salt gave .05562 gram of calcium sulphate.

.01481 gram of the salt gave .0371 gram of calcium sulphate.

For $Ca\left(C_6H_3\begin{<}{CH_3}{SO_3}{O.CH_3}\right)_2$.

	Theory.	Found.
Ca	9.03	9.33–9.38–9.38

Lead Salt.—From a concentrated solution the salt crystallizes in white needles. The salt obtained thus, by crystallization from water, was dissolved in boiling alcohol (98 per cent.). The fact that it dissolved completely, giving a clear solution even after cooling, showed that it was free from lead sulphate. The alcoholic solution was evaporated to dryness and the product again recrystallized from water. So obtained, it gave the following results for water and lead:

.1456 gram of salt gave, at 160°, .0118 gram of water.

.17552 gram of salt gave, at 160°, .01432 gram of water.

.18031 gram of salt gave, at 160°, .08198 gram of lead sulphate.

.2091 gram of salt gave, at 160°, .09505 gram of lead sulphate.

For $Pb\left(C_6H_3\begin{<}{CH_3}{SO_3}{OCH_3}\right)_2.3H_2O$.

	Theory.	Found.
H_2O	8.15	8.10–8.16
Pb	31.16	31.03–31.02

This lead salt, heated on platinum foil, first melts and then burns brilliantly, almost explosively, leaving a residue of carbon which finally burns away, leaving only a black stain on the platinum.

An attempt was made to make the silver salt by dissolving silver oxide in a hot solution of the acid. The salt is obtained in this way, but decomposes easily on boiling or on evaporation over a water-bath, giving a deposit of silver oxide. It was, therefore, not obtained in a pure condition. It was shown to crystallize in needles like the other salts, and to resemble them in its solubility in water and alcohol.

The sodium salt, though not purified, was shown to resemble the other salts in solubility and in its manner of crystallization.

Preparation of Paramethoxymetatoluenesulphonamide.

The amide obtained in the usual way was dissolved in alcohol (92-per cent.), and the solution boiled with animal charcoal, filtered, and evaporated to dryness. The second crystallization from water gave pure white needles, melting at 180°–181°. In

one experiment 18.5 grams of the diazo compound were boiled, under a pressure of 450 mm. of mercury, with 300 cc. of methyl alcohol (distilling at 65°–66°). The yield of purified amide was 4.9 grams, about 26 per cent. of the theoretical. The amide is but very slightly soluble in cold water, and dissolves with difficulty in boiling water. Approximate determinations showed that a liter of water at 10° dissolved about .8 gram of the amide. A liter of boiling water dissolves about 6 grams. The amide is moderately soluble in cold alcohol and ether. The following analyses show the composition of the substance to be $C_8H_{11}O_3NS$:

.27962 gram of the amide gave ammonia equivalent to 13.16 cc. of a standard ammonia solution containing 1.4672 grams of nitrogen to the liter.

.2054 gram of the amide gave .23435 gram of barium sulphate.

.2669 gram of the amide gave .30085 gram of barium sulphate.

.24107 gram of the amide gave .42386 gram of carbon dioxide and .12190 of water.

		For $C_6H_3\begin{cases}CH_3\\SO_2NH_2\\O\,CH_3\end{cases}$.	
		Theory.	Found.
C_8	96	47.76	47.95
H_{11}	11	5.47	5.62
O_3	48	23.88	...
N	14	6.97	6.91
S	32	15.92	15.59 (15.50–15.69)
	201	100.00	

The sulphur determinations were made by Pearson's method, which, as before stated, is liable to give low results.

Besides this methoxy amide there was obtained, by working over the mother-liquors, a small quantity of impure metatoluenesulphonamide. It melted gradually at 94°–108°. It contained the small rhombohedral scales with iridescent reflection so characteristic of this amide. The yield was very small, less than one-tenth of a gram to 4.9 grams of the methoxy amide. The principal reaction with the diazo compound is evidently that in which the nitrogen is replaced by the methoxy group.

Oxidation of Paramethoxymetatoluenesulphonamide.

Four grams of the amide and 1.3 grams of caustic potash, dissolved in 315 cc. of water, were treated with 6.5 grams of potassium

permanganate dissolved in the same amount of water. The mixture was heated on the water-bath about one and a half hours, when the decolorization of the potassium permanganate was complete. The solution was filtered and allowed to cool, when a little over one gram of the unchanged amide crystallized out. The solution, after filtering, contained the potassium salt of the oxidation-product, together with a small amount of the original amide. It was evaporated to a small bulk, and the small amount of amide which crystallized out was separated by filtration. The solution was then diluted to about one half a liter and acidified with hydrochloric acid. The white crystalline precipitate that was obtained was very slightly soluble in cold water, soluble with difficulty in much boiling water. It dissolves easily in cold alcohol. The second recrystallization from water gave a beautiful mass of needles which had all the appearance of a pure substance. It melted, however, with decomposition at 240°–270°. Nitrogen and sulphur determinations also showed plainly that the product was still impure. They differed .3 per cent. and .8 per cent. from the theoretical amount for $C_6H_3\begin{cases}COOH\\SO_2NH_2(m)\\O.CH_3(p)\end{cases}$. They leave little doubt, however, as to the composition of the substance.

Barium Salt.—This salt is quite soluble in water, and crystallizes from a concentrated solution in clusters of pure white needles. It is nearly insoluble in strong alcohol. It was purified by boiling with alcohol (92-per cent.), filtering, and washing thoroughly with cold alcohol. Analyses showed the composition to be

$$Ba\left(C_6H_3\begin{cases}CO_2\\SO_2NH_2\\O.CH_3\end{cases}\right)_2.3H_2O.$$

.1508 gram of the salt gave, at 250°, .01209 gram of water and .0541 gram of barium sulphate. This gives, for the percentage of water, 8.02; theory, 8.29; and for the percentage of barium, 21.03; theory, 21.04.

	Theory.	Found.
H_2O	8.29	8.02
Ba	21.04	21.03

The last molecule of water of crystallization was given off only by long heating at high temperatures. Without this last molecule

the salt was excessively hygroscopic, so that it was very difficult to get an accurate weight.

The attempt was made to get the pure acid by precipitating it from the barium salt with hydrochloric acid. The specimen obtained in this way was probably pure, but it still melted with decomposition at 240°–270°. It will be remembered that the corresponding ethoxy acid, although pure, behaved in a similar way. No further analysis was made of the acid, as the material was needed for other experiments.

Action of Propyl Alcohol on Paradiazometatoluenesulphonic Acid.

It appears, from what has been said, that when the diazo compound under consideration—$C_6H_3\begin{cases}CH_3\\SO_3(m)\\N_2(p)\end{cases}$—is boiled under pressure with methyl or ethyl alcohol, the principal reaction that takes place is that in which the diazo group is replaced by the alkoxy group. It was thought of interest to determine whether the analogous reactions could be obtained with other alcohols. The action of propyl alcohol was tried and gave similar results.

Seventeen grams of the diazo compound were boiled with 250 cc. of propyl alcohol under a pressure of 200–220 mm. of mercury for about twenty minutes. The diazo compound was completely dissolved, giving a dark red solution, much darker than that obtained with the methyl or ethyl alcohol. The solution was neutralized with dry sodium carbonate and evaporated to dryness on a water-bath. A dark, gummy mass was left, which did not harden after long drying at 110° in an air-bath. On cooling, however, the mass became hard and could be pulverized. To the pulverized material was added an equal weight of phosphorus pentachloride. This gave a dark brown, gummy oil. By washing and treating with concentrated ammonia in the usual way, the crude amide was obtained in the form of a dark brown mass. This was washed with water and dissolved in alcohol. Boiling with animal charcoal failed to lighten the dark red color of the alcoholic solution. The solution was evaporated to dryness and the residue dissolved, boiled with animal charcoal, and recrystallized from water five times. In this way 1.6 grams of the pure white material were obtained. The melting-point was 126.5°–128°. The substance is nearly insoluble in cold water, moderately

soluble in boiling water, easily soluble in alcohol. It crystallizes in needles.

The following analyses show the composition of the substance to be $C_{10}H_{15}O_3NS$:

.19488 gram of the amide gave ammonia equivalent to 7.99 cc. of a standard ammonia solution containing 1.4672 grams of nitrogen to the liter.

.1337 gram of the amide gave .13397 gram of barium sulphate.

.26792 gram of the amide gave .5139 gram of carbon dioxide. The water was lost.

		For $C_{10}H_{15}O_3NS$. Theory.	Found.
C_{10}	120	52.40	52.31
H_{15}	15	6.55	...
O_3	48	20.96	...
N	14	6.11	6.02
S	32	13.97	13.97
	229	99.99	

Besides the propoxy amide a very small quantity of a substance having a low melting-point was obtained from the last mother-liquors. The amount was too small to admit of purification. It did not crystallize like the ordinary metatoluenesulphonamide, but in all probability it contained this compound. It was undoubtedly produced in less quantity than the propoxy compound. The yield of the latter, however, as has been seen, was very small, 17 grams of the diazo compound giving only 1.6 grams of the purified amide, or about 7.8 per cent. of theoretical. It is to be remembered that the actual yield was several times greater than this, loss being inevitable in repeated crystallizations of small amounts.

Pressure Experiments.

The experiments described above show that when paradiazometatoluenesulphonic acid is decomposed with methyl, ethyl, or propyl alcohol under a pressure of 200 mm. or more, the diazo group is replaced by the alcoholic group to a much greater extent than by hydrogen. Some experiments were performed in order to get an insight into the question of what influence, if any, pressure exerts on the course of the reaction. Time and material were lacking for an exhaustive study of this question, but the few preliminary experiments performed have some value.

Three lots of the diazo compound, of ten grams each, were treated in exactly the same way, with the one exception that one was decomposed at 200, the second at 400, the third at 600 mm. pressure. The ten grams were placed in the dry pressure-flask and 250 cc. of absolute methyl alcohol were added. The alcohol was then boiled, under pressure, for thirty minutes. Nitrogen was freely given off and the diazo compound was dissolved, giving a clear solution of an orange-yellow color. This was poured from the flask without rinsing, neutralized with 4.9 grams of dry sodium carbonate, and evaporated to dryness on a water-bath. About 11 grams of the pinkish white sodium salt were obtained. After cooling, 11 grams of phosphorus pentachloride were added. A red oil was thus obtained which, on cooling, solidified less perfectly than in some previous experiments. This chloride was washed in 1½ liters of cold water, each of the three lots being treated in exactly the same way. The same quantity of concentrated ammonium hydrate was then added to each. The material was allowed to stand in contact with the ammonia solution over night and then evaporated to dryness on a water-bath. The three lots of crude amide so obtained were boiled in the same quantity of distilled water. Each left a small residue of tarry matter. They were filtered through filter-papers of the same size, boiled with the same amount of animal charcoal, and again filtered through the same filters. The dishes and filters were rinsed with the same amount of boiling water. On cooling, a fairly pure specimen of methoxyamide was deposited in each case. That which had been decomposed at 200 mm. pressure and 71°–72° temperature gave 1.145 grams of the amide, or 11.28 per cent. of theoretical; that decomposed at 400 mm. pressure and 75°–76° temperature gave 1.325 grams of the amide, or 13.05 per cent.; that decomposed at 600 mm. pressure and 81° temperature gave 1.51 grams of the amide, or 14.88 per cent. The pressures were not kept perfectly constant but varied occasionally as much as 10 mm. each side of the figures given.

The amounts obtained do not represent the entire yield, as the mother-liquors were not worked over and the animal charcoal was not boiled to dissolve out the amide clinging to it. The mother-liquors and the animal charcoal were afterwards put together and from them a considerable additional quantity of the amide obtained. The figures given above, however, must represent very

closely the relative yield in each case, since the loss in each case must have been very nearly identical. The experiments show that an increase of pressure increases the yield of the methoxy compound.[1]

Some experiments, tried in essentially the same way with absolutely anhydrous ethyl alcohol, proved less satisfactory. The alcohol used was shown both by its method of formation, by its specific gravity, and by analysis to be entirely pure anhydrous alcohol. The odor of aldehyde was strong during each of the three experiments, and the relative yield of the ethoxy amide was so small, and the substance so mixed with the metatoluenesulphonamide and with an oily substance, that it proved impossible to separate it in such a way as to obtain any definite results. The appearance of the material indicated that the lot boiled at 600 mm. contained a considerably larger amount of the ethoxy compound than the others.

VI.—THE ACTION OF METHYL ALCOHOL ON PARADIAZO-ORTHOTOLUENESULPHONIC ACID.[2]

By R. M. Parks.

Comparatively few experiments have been made on the decomposition of diazo compounds by methyl alcohol, and these indicate that the decomposition generally yields the methoxy product. Hofmann[3] observed that the diazo compound obtained from amidine yields the methyl ether of trimethylbenzene. He also obtained anisol from diazobenzene and methyl alcohol. Griess[4] has shown that meta- and paradiazobenzoic acids give respectively metamethoxy- and paramethoxybenzoic acids, while the ortho acid gives benzoic acid. Metcalf[5] has shown that with methyl alcohol, paradiazometatoluenesulphonic acid yields mainly the corresponding methoxytoluenesulphonic acid.

Hayduck,[6] in decomposing the diazo compound of orthoamidoparatoluenesulphonic acid with methyl alcohol, obtained at ordinary pressure the methoxy product, namely, orthomethoxyparatoluenesulphonic acid, or, as Hayduck named it, methylcresolsulphonic acid.

[1] See Remsen and Dashiell: This Journal **15**, 105.

[2] From the author's thesis for the degree of Doctor of Philosophy. Presented to the Board of University Studies of the Johns Hopkins University, June, 1892.

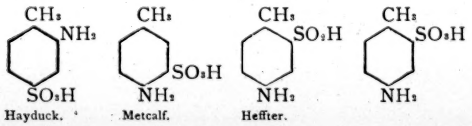
[3] Ber. d. chem. Ges. **17**, 1917.

[4] *Ibid.* **21**, 978.

[5] See preceding article.

[6] Ann. Chem. (Liebig) **172**, 217.

Limpricht and Heffter,[1] from the diazo compound derived from paraamidoorthotoluenesulphinic acid and methyl alcohol, obtained paramethoxyorthotoluenesulphonic acid. This acid is apparently identical with the acid obtained in this investigation, and they are compared in the succeeding pages. The formulas of the amido acids from which the diazo compounds were derived are given here. The last is of the one used in this investigation, which I have undertaken at the suggestion and carried on under the direction of Professor Remsen.



Hayduck. Metcalf. Heffter.

The paratoluidineorthosulphonic acid used in the experiments to be described was prepared according to the directions of Beilstein and Kuhlberg,[3] and of Brackett and Hayes.[5] From this the diazo compound was prepared according to the directions given by de Roode.[4]

Decomposition of the Diazo Compound with Methyl Alcohol.

A preliminary experiment at ordinary pressure was made and it was found that the diazo compound decomposed without difficulty. On evaporating the solution a dark heavy liquid having an acid reaction remained. This acid was converted into the barium salt by treatment with pure barium carbonate. On evaporation of the water solution there were deposited large tabular crystals together with a white powder. This result seemed to indicate the formation of two products, as in the decomposition with ethyl alcohol as described by Remsen and Dashiell.[6]

Three experiments were made under like conditions, that is, at ordinary pressure, with absolute methyl alcohol. In each case ten grams of the diazo compound were boiled with 200 cc. of absolute methyl alcohol in an Erlenmeyer flask connected with an inverted condenser. The decomposition began when the boiling of the alcohol commenced. That a decomposition was occurring was

[1] Ann. Chem. (Liebig) **221**, 344.
[2] Ann. Chem. (Liebig) **155**, 8.
[3] This Journal **9**, 399.
[4] This Journal **13**, 217.
[5] This Journal **8**, 105.

indicated by the change of color of the liquid and the escape of gas. The color was at first cherry-red, and at the end of the decomposition reddish brown. The reaction was complete in about one hour and fifteen minutes. By this time all solid matter had disappeared and the methyl alcohol simply boiled without the evolution of gas. Each portion was then connected with an ordinary condenser and the alcohol distilled from the product of decomposition. As in the preliminary experiment the acid residue was converted into the barium salt by means of pure barium carbonate. The water solution of the barium salt was evaporated to dryness and dried in the air-bath at 100°.

Experiment I. 10 grams of diazo compound gave 13.54
" II. 10 " " " 13.49
" III. 10 " " " 13.51
grams of barium salt.

The three portions were again dissolved in water and evaporated to crystallization. There first appeared a nearly white, not well crystallized salt, and then well crystallized, yellowish, sometimes reddish brown, tables. An attempt was made to separate the two salts by means of alcohol, as was done by Remsen and Dashiell,[1] but this did not prove satisfactory. In order to get material for immediate analysis, the well crystallized portion was separated mechanically from the white powder. The tabular crystals were first analyzed. The salt begins to lose water at 60°; at from 110° to 150° the weight is constant. The loss in weight corresponds closely to the loss of two molecules of water from the compound. On further heating to 165° the third and last molecule of water of crystallization was driven off, and higher heating did not produce any further loss. The analysis gave the following results:

I. 0.2530 gram of salt lost at 165° 0.0230 gram of water and gave 0.0990 gram of barium sulphate.

II. 0.2386 gram salt lost 0.0216 gram of water and gave 0.0937 gram of barium sulphate.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2 Ba.3H_2O$.	Found. I.	Found. II.
H_2O	9.11	9.09	9.05
Ba	23.13	23.02	23.10

[1] *Loc. cit.*

Estimations of barium were now made both with the non-crystallized portion and also with the mixture of the well crystallized and non-crystallized which could not be separated mechanically. In the case of the white powder, or non-crystallized portion, it was not possible to determine water of crystallization. The results did not agree with each other. The analyses were made from the white powder and the mixture, after dehydrating at 165°, and gave the following results:

I. 0.2060 gram of the powder gave 0.0892 gram of barium sulphate.

II. 0.2399 gram of the powder gave 0.1043 gram of barium sulphate.

III. 0.2086 gram of the mixture gave 0.0896 gram of barium sulphate.

IV. 0.2541 gram of the mixture gave 0.1091 gram of barium sulphate.

If the hydrogen reaction had taken place at all, the barium salt of orthotoluenesulphonic acid should have been present. The comparison of the percentages of barium in the above four analyses with the percentage of barium in barium orthotoluenesulphonate and in barium paramethoxyorthotoluenesulphonate would give a strong indication as to the course of the reaction. The calculated percentages are for the anhydrous salts —

	Calculated for $\left(C_6H_4<\begin{matrix}CH_3\\SO_3\end{matrix}\right)_2Ba$.	Calculated for $\left(C_6H_3<\begin{matrix}CH_3\\SO_3\\OCH_3\end{matrix}\right)_2Ba$.	Found. I.	II.	III.	IV.
Ba	28.63	25.44	25.47	25.58	25.26	25.26

These analyses furnish no evidence that the hydrogen reaction had taken place. If it had occurred at all, it was to so small a degree as to escape detection by analysis. Further, in collecting the gas given off during the decomposition, no evidence could be obtained of the presence of formaldehyde. The gas was nitrogen only. The different portions which had been analyzed for barium with the results stated above were changed into the sodium salt. This sodium salt was treated with phosphorus pentachloride. The acid chloride thus formed was transformed into the amide by means of strong aqueous ammonia. There resulted only one amide melting at 150°. In fact all the derivatives and transformations subsequently made furnish additional evidence that there

was only one product formed. This product at ordinary pressure is paramethoxyorthotoluenesulphonic acid.

Experiment at Increased Pressure.

In order to study the influence of pressure on the course of the reaction, one experiment was made at an increased pressure of 200 millimeters and one experiment at a diminished pressure. The experiment at increased pressure was conducted in the apparatus used and described by Remsen and Dashiell.[1]

Ten grams of the diazo compound were decomposed with absolute methyl alcohol in the pressure-flask at 200 millimeters pressure. The same phenomena were observed as at ordinary pressure, only the decomposition was complete in about forty-five minutes. The barium salt made from the acid produced appeared like that formed from the product of decomposition at ordinary pressure. Analyses were made of the barium salt dehydrated at 165°, no attempt being made at separation. The results of analysis are as follows:

I. 0.1870 gram of substance gave 0.0809 gram of barium sulphate.

II. 0.2153 gram of substance gave 0.0928 gram of barium sulphate.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Ba$.	Found. I.	Found. II.
Ba	25.44	25.44	25.36

The only product of the reaction is therefore methoxytoluenesulphonic acid.

Experiment at Diminished Pressure.

An experiment was made at one-half atmosphere pressure also. The apparatus consisted of a strong one-liter balloon flask fitted with a three-hole rubber stopper. In one hole was a bent glass tube connected with a vacuum-gauge. Through the second ran a thermometer. The tube of an upright condenser passed through the third hole. Into the upper end of the condenser was fastened, by means of a one-hole rubber stopper, the short arm of a twice-bent glass tube, the long arm of which terminated a few millimeters below a two-hole rubber stopper in a filtering flask. A test-tube

[1] *Loc. cit.*

was placed upright within the flask, the open end being immediately below around the end of the long arm of the tube connected with the condenser. This tube served to collect the methyl alcohol should any distil over during the experiment. Through the second hole of the stopper in the filtering flask passed a bent glass tube, one end terminating in the bottom of the flask, the other end connected with a Bunsen suction-pump. By this means, if water should be drawn into the flask from the pump, it would not interfere with the experiment, and on admitting air into the apparatus the tube terminating in the bottom would conduct the water off completely. The pressure inside the apparatus was regulated by attaching a rubber tube to the side tube of the filtering flask and closing the rubber tube with a Mohr pinchcock. The pressure could then be regulated by hand. By carefully watching the vacuum-gauge or the thermometer the pressure could be kept constant for any length of time, *i. e.*, without a variation of more than 20 millimeters of pressure or 2° of temperature.

The diazo compound and absolute methyl alcohol were introduced into the flask, the pump turned on, and at one-half atmosphere pressure the flask was heated in a water-bath. The decomposition proceeded much more slowly than in previous experiments. The methyl alcohol boiled at 49°–51°, the pressure being about 380 millimeters.

Ten grams of diazo compound required six and one-half hours for complete decomposition. The methyl alcohol was distilled from the product of decomposition, barium carbonate added, and the barium salt evaporated to dryness, dehydrated, and analyzed for barium with the following results:

I. 0.1538 gram of the substance gave 0.0668 gram of barium sulphate.

II. 0.1933 gram of substance gave 0.0835 gram of barium sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\OCH_3\end{cases}\right)_2Ba$.	Found. I.	II.
Ba	25.44	25.55	25.41

As in the cases with ordinary and increased pressure, only one product could be obtained and this was the methoxy compound. Variation of pressure does not change the course of the reaction.

Paramethoxyorthotoluenesulphonic Acid.

In all subsequent experiments larger amounts of the diazo compound were decomposed with methyl alcohol. To one hundred grams of the diazo compound one liter of methyl alcohol was used. The product after distilling the methyl alcohol is a dark brown liquid easily soluble in alcohol and water. Made in large quantities it shows signs of crystallization after standing twenty-four hours. Set aside for several weeks it solidifies, but not in well-defined crystals. Boiling with animal charcoal does not entirely remove the color. After many attempts a small quantity of the acid was obtained in well-defined rhombohedral plates of a yellowish brown color. The acid decomposes without melting. The acid purified as far as possible with animal charcoal or the acid derived from the well-crystallized barium salt, was used for making salts.

Barium salt, $\left(C_6H_3\begin{cases}CH_3\\ -SO_3\\ OCH_3\end{cases}\right)_2Ba.3H_2O$.—Analyses of this salt have already been given. It crystallizes from concentrated water solution in large monoclinic tabular crystals with three molecules of water of crystallization. Only the well-crystallized is formed from the hot solution of thirty parts of salt in one hundred parts of water. If the concentration is greater than this the salt is first deposited from the hot solution in the form of a white powder having less than three molecules of water of crystallization. Since the crystals begin to lose water at 60° (also by standing in the air at ordinary temperature), it appears that even in boiling water at a certain concentration the salt loses some of its water of crystallization, probably two molecules. The salt is easily soluble in water, difficultly soluble in alcohol.

Calcium salt, $\left(C_6H_3\begin{cases}CH_3\\ -SO_3\\ OCH_3\end{cases}\right)_2Ca.4H_2O$.—This salt, prepared by neutralization of the free acid with finely powdered calcite, is exceedingly soluble in water, less so in alcohol. From water it forms a compact mass of lustrous, transparent crystals. Analysis for calcium and water gave the following results:

I. 0.2755 gram of the salt lost at 170° 0.0383 gram of water and gave 0.0726 gram of calcium sulphate.

II. 0.2402 gram of the substance lost 0.0335 gram of water and gave 0.0617 gram of calcium sulphate.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Ca.4H_2O$.	Found. I.	II.
H_2O	14.01	13.90	13.94
Ca	7.78	7.77	7.58

Magnesium salt, $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Mg.5H_2O$.—This salt, prepared by neutralization of the free acid with pure magnesium carbonate, is very soluble in water and in alcohol. From water it crystallizes in radial tufts of short slender prisms; from alcohol, in white plates. Analysis for magnesium and water gave the following results:

I. 0.3192 gram of the salt lost at 140° 0.0545 gram of water and gave 0.0769 gram of magnesium sulphate.

II. 0.2174 gram of substance lost 0.0376 gram of water and gave 0.0495 gram of magnesium sulphate.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Mg.5H_2O$.	Found. I.	II.
H_2O	17.44	17.07	17.30
Mg	4.65	4.81	4.55

Zinc salt, $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Zn.6H_2O$.—This is prepared by neutralization of the free acid with pure zinc carbonate. The salt is easily soluble in alcohol and in water; crystallizes in short, pointed prisms. Analysis for zinc and water gave the following results:

I. 0.2491 gram of salt lost at 165° 0.0466 gram of water and gave 0.0344 gram of zinc oxide.

II. 0.2791 gram of substance lost 0.0526 gram of water and gave 0.0387 gram of zinc oxide.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CH_3\\SO_3\\OCH_3\end{smallmatrix}\right)_2Zn.6H_2O$.	Found. I.	II.
H_2O	18.77	18.71	18.85
Zn	11.34	11.09	11.14

Sodium salt, $C_6H_3(CH_3)(OCH_3)SO_3Na.1\frac{1}{2}H_2O$.—This is prepared by exact precipitation of the metal from the barium salt with a solution of sodium carbonate. It is extremely soluble in water and in alcohol. When evaporated almost to dryness, the solution, on cooling, solidifies to a compact mass of almost colorless leaflets. Analysis gave the following results:

I. 0.2844 gram of salt lost at 160° 0.0304 gram of water and gave 0.0811 gram of sodium sulphate.

II. 0.2863 gram of substance lost 0.0303 gram of water and gave 0.0820 gram of sodium sulphate.

	Calculated for $C_6H_3(CH_3)(OCH_3)SO_3Na.1\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	10.75	10.69	10.58
Na	9.18	9.25	9.29

Potassium salt, $C_6H_3(CH_3)(OCH_3)SO_3K.H_2O$.—This is prepared by exact precipitation of the metal from the barium salt by a solution of potassium carbonate. It is very soluble in water and in alcohol. From the hot concentrated solution there is deposited a mass of almost colorless, fine branching needles. Analysis for potassium and water gave the following results:

I. 0.2297 gram of the salt lost 0.0160 gram of water and gave 0.0771 gram of potassium sulphate.

II. 0.2319 gram of substance lost 0.0165 gram of water and gave 0.0777 gram of potassium sulphate.

	Calculated for $C_6H_3(CH_3)(OCH_3)SO_3K.H_2O$.	Found.	
H_2O	6.97	6.97	7.12
K	15.11	15.07	15.04

Paramethoxyorthotoluenesulphonic chloride, $C_6H_3(CH_3)(1)(OCH_3)(4)SO_2Cl$ (2).—To the dried and powdered sodium salt a slight excess by weight of phosphorus pentachloride was added. The reaction soon began and proceeded with violence and with evolution of consid-

erable heat. Most of the phosphorus oxychloride was driven off by the heat of the reaction. The last portions of the oxychloride, held back by the sodium chloride, could not be entirely removed even when heated to 120°. After cooling the acid chloride was poured into a large amount of cold water and washed. The chloride is a heavy oil, yellowish white in color, very soluble in ether, from which it was not obtained in crystalline form, but reappeared as an oil after the slow evaporation of the ether.

Paramethoxyorthotoluenesulphonamide, $C_6H_3\begin{cases}CH_3\\OCH_3\end{cases}SO_2NH_2$.—This was prepared by treating the acid chloride with strong aqueous ammonia. The reaction began at once, the aqueous ammonia soon began to boil vigorously, and after shaking for a short time the amide suddenly solidified into a grayish white mass. After evaporating off the excess of ammonia on the water-bath and acidifying with hydrochloric acid, the amide was filtered and washed with cold water. The amide is very soluble in alcohol, in which it is best dissolved and decolorized with animal charcoal. It is then deposited from the hot concentrated alcoholic solution as white plates. The amide is difficultly soluble in cold and in hot water. From boiling water it crystallizes in quadratic plates if rapidly cooled; if slowly, in short, pointed prisms with a vitreous lustre. The amide is soluble in ammonia and in the alkaline carbonates, from which it is precipitated on addition of acids. The pure amide melts at 151°. Not a trace of the amide of orthotoluenesulphonic acid was obtained from the mother-liquors. Analysis for sulphur and nitrogen gave the following results:

I. 0.3471 gram of the amide gave 0.4044 gram of barium sulphate.

II. 0.3177 gram of the amide gave 0.3720 gram of barium sulphate.

III and IV. Determinations of nitrogen (Kjeldahl).

	Calculated for $C_6H_3\begin{cases}CH_3\\OCH_3\end{cases}SO_2NH_2$.	Found. I.	II.
S	15.94	16.01	16.09
		III.	IV.
N	6.98	6.79	6.90

Comparison with the Oxymethyltoluenesulphonic Acid of Limpricht and Heffter.[1]

Heffter, when studying paraamidotolueneorthothiosulphonic acid, had changed this thiosulphonic acid into the corresponding sulphinic acid. On diazotizing the paraamidoorthotoluenesulphinic acid, and decomposing the diazo compound in absolute methyl alcohol, he obtained a non-crystallizing acid which he called oxymethyltoluenesulphonic acid. To this he gave the formula $C_6H_3\begin{cases}CH_3 & (1)\\ SO_2H & (2)\\ OCH_3 & (4)\end{cases}$. This acid is apparently identical with the product described above. As Heffter's description of the acid, its barium and potassium salts, did not agree in all particulars with the description of compounds of like composition and constitution already given in this article, it was thought advisable to repeat his experiments for the purpose of comparison. The starting-point of Heffter's experiments was paranitroorthotoluenesulphonic acid. The chloride of this acid, made by treating the potassium salt with phosphorus pentachloride and crystallizing from ether, when treated with acid ammonium sulphide passes over into the ammonium salt of paraamidoorthotoluenethiosulphonic acid, according to the equation:

$$C_7H_6\begin{cases}NO_2\\ SO_2Cl\end{cases} + 4NH_4HS =$$

$$C_7H_6\begin{cases}NH_2\\ SO_2SNH_4\end{cases} + NH_4Cl + 2NH_3 + 2H_2O + 3S.$$

After concentration of the liquid and removal of the separated sulphur, the difficultly-soluble free thiosulphonic acid is precipitated by acetic acid.

This reaction was performed and the acid obtained as described, in hard, yellowish prisms. The change to the sulphinic acid is effected by boiling with hydrochloric acid or by means of sodium amalgam. Heffter advises the use of sodium amalgam. Therefore fifteen grams of the sodium salt of the thiosulphonic acid were reduced by about 600 grams of sodium amalgam, made by bringing together 600 grams of mercury and 20 grams of metallic sodium. By this reduction the sulphur of the group SH is

[1] Ann. Chem. (Liebig) **221**, 344.

changed to hydrogen sulphide. Addition of acetic acid precipitated the sulphinic acid $C_6H_3\begin{cases}CH_3 & (1)\\ SO_2H & (2).\\ NH_2 & (4)\end{cases}$

Crystallized from hot water the acid was obtained in colorless, hard prisms. The diazo compound of the sulphinic acid was made by Heffter, by passing nitrous acid into well-cooled absolute alcohol in which the finely divided sulphinic acid was suspended. The diazo compound forms yellow to brown needles, which are soon colored dark in the air. Water and alkalies decompose it at ordinary temperatures, with separation of a brown resin insoluble in alcohol and in ether. Some of the acid was suspended in absolute methyl alcohol, well cooled; then nitrous fumes were passed through. The diazo compound appeared in a short time as brown needles. These were quickly filtered and washed a few times with methyl alcohol. The diazo compound was then placed in a flask with methyl alcohol; the reaction proceeded at ordinary temperature. On warming on the water-bath the reaction was complete in a short time. Water was added, the precipitated mass filtered off, and the filtrate evaporated on the water-bath. Barium carbonate was then added, the barium salt filtered from the excess of barium carbonate and evaporated to dryness. A portion of the dried salt was dissolved in absolute alcohol by boiling. After cooling, addition of ether precipitated the salt as a yellowish powder, as described by Heffter. So far the work of Heffter was repeated.

Efforts were now made to obtain the salt in crystallized form by crystallizing from water. The dried barium salt, also the portion precipitated by ether from the alcoholic solution, were dissolved in water and boiled with animal charcoal. After filtering, the solution of the salt was bright yellow in color. It was evaporated to crystallization. On cooling of the concentrated solution there first appeared a white powder, then well-defined crystals like the barium salt described at the beginning of this article. The yield of barium salt was very small, twelve grams of the sulphinic acid giving but little more than one gram of the barium salt of the methoxy acid. Heffter says that eight grams of the sulphinic acid gave only one gram of the pure barium salt of the ethoxy acid, while the yield of the methoxy salt was still smaller. One analysis was made for barium and water, and one for barium only, in the dehydrated salt.

I. 0.2588 gram of the salt lost at 165° 0.0232 gram of water and gave 0.1036 gram of barium sulphate.

II. 0.2739 gram of dehydrated salt gave 0.1202 gram of barium sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\OCH_3\end{cases}\right)_2 Ba.3H_2O$.	Found. I.	Found. II.
H_2O	9.11	8.96	...
Ba	23.13	23.55	...
Dehydrated salt:			
Ba	25.44	25.87	25.89

The differences are now narrowed down to the crystallizing power of the acid. But it must be said that only when working with large quantities of the acid is it possible to detect any signs of crystallization. As Limpricht and Heffter worked only with a very small quantity of the acid, it is not surprising that it was not obtained crystallized.

The conclusion seems to be justified that the two methoxy acids are identical. Whether the diazo compounds from which the acids are derived are identical or not is a question to which an answer is not attempted at this time.

Action of Potassium Permanganate on Paramethoxyorthotoluenesulphonamide.

10 grams of paramethoxyorthotoluenesulphonamide, 40 grams of potassium permanganate with one liter of water were placed in a one and one-half liter flask, sunk in water and heated for some hours at the boiling temperature of water. The color of the permanganate disappeared in about three hours. The solution was then filtered from the insoluble manganese compounds and evaporated to a small volume. Addition of hydrochloric acid produced a white precipitate of fine needles. After filtering and washing the precipitate in cold water it was dissolved in boiling alcohol. The compound is easily soluble in hot alcohol, difficultly in cold. Any unoxidized amide is thus easily separated, as it is quite soluble in cold alcohol. From alcohol the methoxybenzoic sulphinide crystallizes in beautiful long, blade-like crystals, difficultly soluble in boiling water. On cooling of the water solution, long slender needles four to six centimeters in length appear. The crystals melt at 271°.

Analyses for sulphur and nitrogen show the compound to be paramethoxybenzoic sulphinide. The following are the results of analysis:

I. 0.1654 gram of the substance gave 0.1806 gram of barium sulphate.

II. 0.1833 gram of the substance gave 0.2025 gram of barium sulphate.

III and IV. Determinations of nitrogen after Kjeldahl (Gunning modification).

	Calculated for $C_6H_3\begin{cases}CO\\SO_2NH\\OCH_3\end{cases}$.	Found. I.	II.
S	15.04	15.00	15.18
		III.	IV.
N	6.59	6.47	6.74

Barium salt of methoxybenzoic sulphinide,

$\left(C_6H_3\begin{cases}CO\\SO_2N\\OCH_3\end{cases}\right)_2Ba.3H_2O$.—Two grams of methoxybenzoic sulphinide were dissolved in boiling water and pure barium carbonate added. After boiling some time the excess of barium carbonate was filtered off and the filtrate evaporated to a small volume. The salt is easily soluble in water, from which it crystallizes in long colorless needles concentrically arranged. The air-dried salt was washed with absolute alcohol, recrystallized from water, and analyzed for water of crystallization and barium with the following results:

I. 0.2438 gram of the salt lost 0.0215 gram of water and gave 0.0920 gram of barium sulphate.

II. 0.1860 gram of the substance lost 0.0166 gram of water and gave 0.0701 gram of barium sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CO\\SO_2N\\OCH_3\end{cases}\right)_2Ba.3H_2O$.	Found. I.	II.
H_2O	8.78	8.82	8.92
Ba	22.29	22.19	22.17

Acid potassium salt of paramethoxyorthosulphobenzoic acid,

$C_6H_3\begin{cases}CO_2H\\SO_2K.H_2O\\OCH_3\end{cases}$.—If the filtrate from methoxybenzoic sulphinide be evaporated almost to dryness, potassium chloride first crys-

tallizes, then long beautiful prisms, almost colorless, which proved to be the acid potassium salt of paramethoxyorthosulphobenzoic acid. The salt can be obtained from these mother-liquors either by fractional crystallization to free it from potassium chloride, or by evaporating to dryness and extracting with alcohol. The salt is much more soluble in alcohol than potassium chloride, and may thus be obtained quite pure. Analysis of the salt gave the following results:

I. 0.2628 gram of the salt lost at 125° 0.0166 gram of water and gave 0.0786 gram of potassium sulphate.

II. 0.2224 gram of dehydrated salt gave 0.0714 gram of potassium sulphate.

	Calculated for $C_6H_3\begin{cases}CO_2H\\SO_3K.H_2O\\OCH_3\end{cases}$.	Found. I.	Found. II.
H_2O	6.25	6.32	...
K	13.58	13.43	...
Dehydrated salt:			
K	14.44	...	14.41

The acid potassium salt was made also by oxidizing the potassium salt of paramethoxyorthotoluenesulphonic acid. Ten grams of this salt were dissolved in 1 liter of water, 15 grams of potassium permanganate added, and the solution heated in boiling water. The color of the permanganate disappeared in about two hours. After removing the insoluble manganese compounds and evaporating to a small volume, strong hydrochloric acid throws down the acid potassium methoxysulphobenzoate as short needles. These needles, recrystallized from water and analyzed, gave the following results:

I. 0.2766 gram of the salt lost 0.0174 gram of water and gave 0.0842 gram of potassium sulphate.

II. 0.2763 gram of dehydrated salt gave 0.0894 gram of potassium sulphate.

	Calculated for $C_6H_3\begin{cases}CO_2H\\SO_3K.H_2O\\OCH_3\end{cases}$.	Found. I.	Found. II.
H_2O	6.25	6.29	...
K	13.58	13.66	...
Dehydrated salt:			
K	14.44	...	14.49

Acid barium salt, $\left(C_6H_3\begin{cases}CO_2H\\SO_3-\\OCH_3\end{cases}\right)_2 Ba.4H_2O$.—This was prepared from the free methoxysulphobenzoic acid. A water solution of the acid was divided into two equal parts; one part was neutralized with barium carbonate. To this neutral barium salt the second part of the acid was added to produce the acid salt. Both the neutral and acid salts are extremely soluble in water and were not obtained in crystals. In hydrochloric acid the acid barium salt is difficultly soluble, and from it it crystallizes in fine white needles. Analysis gave the following results:

0.2212 gram of the salt lost at 180° 0.0234 gram of water and gave 0.0761 gram of barium sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CO_2H\\SO_3-\\OCH_3\end{cases}\right)_2 Ba.4H_2O$.	Found.
H_2O	10.72	10.58
Ba	20.44	20.24

Paramethoxyorthosulphobenzoic acid, $C_6H_3\begin{cases}CO_2H\ (1)\\SO_3H\ (2)\\OCH_3\ (4)\end{cases}$.—This acid was first prepared from the acid potassium salt by converting the salt into the chloride by means of phosphorus pentachloride, then decomposing the acid chloride in boiling water, evaporating to dryness and recrystallizing from water. A second method is to pass from the methoxybenzoic sulphinide to the acid. This is accomplished by boiling the methoxybenzoic sulphinide in dilute hydrochloric acid, one part of the concentrated acid to eight parts of water. As in the case of benzoic sulphinide, the acid ammonium salt of the corresponding acid is formed. The acid ammonium salt when treated with twice its weight of phosphorus pentachloride gives the chloride. When this chloride is boiled with water, hydrochloric acid is given off and the acid is formed. Crystallized from water, in which it is quite soluble, this acid appears as long, interlacing needles, transparent and colorless. It melts without decomposition at 104°. On cooling it quickly solidifies, and when again heated melts at the same point. This may be repeated without change of the melting-point.

Chloride of paramethoxyorthosulphobenzoic acid, $C_6H_3\begin{cases}COCl\\SO_2Cl.\\OCH_3\end{cases}$—The chloride prepared as above described for the preparation

of the methoxysulphobenzoic acid is a white solid. It does not dissolve easily in ether. From ether it crystallizes in small, hard crystals, transparent and colorless. The crystals powdered and boiled with aqueous ammonia give the methoxybenzoic sulphinide melting at 271°.

Comparison of Paramethoxyorthosulphobenzoic Acid with the Sulphanisic Acid of Zervas.[1]

Anisic acid, $C_6H_4\begin{cases}COOH\ (1)\\OCH_3\ (4)\end{cases}$, according to the theory, should give two sulphonic acids, one with the sulphonic acid group in the ortho position to carboxyl, the other with this group in the meta position to carboxyl:

$$C_6H_3\begin{cases}COOH\ (1)\\SO_3H\ (2)\\OCH_3\ (4)\end{cases} \quad \text{and} \quad C_6H_3\begin{cases}COOH\ (1)\\SO_3H\ (3)\\OCH_3\ (4)\end{cases}.$$

By derivation the acid described in this paper should be expressed by the first of these formulas. It was thought advisable to repeat the experiments as follows: 5 grams of crystallized anisic acid in a small Erlenmeyer flask were covered with fuming sulphuric acid and heated in a water-bath for two hours. After cooling, the contents of the flask were poured into cold water. This solution of sulphanisic acid and the excess of sulphuric acid was neutralized with pure lead carbonate. The lead salt as described by Zervas was found to crystallize from hot water in beautiful transparent crystals. It was transformed into the sodium salt by precipitation of the metal with a solution of sodium carbonate. A portion of this salt was fused with potassium hydroxide, and thus converted into protocatechuic acid, which was crystallized from ether. A portion of the crystals was dissolved in water, and this solution gave the characteristic color reaction with ferric chloride, namely, dark green. Addition of a very little sodium carbonate changed the green color to blue, passing rapidly into red. The melting-point of the needles from ether was found to be 194°.

Some of the methoxybenzoic sulphinide was fused with potassium hydroxide also. The products were resorcin and 1, 2, 4-dioxybenzoic acid. Both were recognized by their melting-

[1] Ann. Chem. (Liebig) **103**, 338.

points and by the reaction with ferric chloride. It is therefore clear that the methoxy acid described in this article is not identical with the sulphanisic acid of Zervas, and that in the latter the sulphonic-acid group is in the meta position with reference to the carboxyl.

Summary.

I. When paradiazoorthotoluenesulphonic acid is decomposed with absolute methyl alcohol at ordinary, increased, or diminished pressure, only the methoxy product is formed, namely, para-methoxyorthotoluenesulphonic acid.

II. This result does not conform to the rules deduced from the study of the decomposition of diazo compounds with ethyl alcohol, but does confirm the suggestion that the simpler alcoholic group is introduced more easily than more complex ones.

III. The product of the reaction is identical with the oxy-methyltoluenesulphonic acid obtained by Limpricht and Heffter in the decomposition of the diazo compound from paraamido-orthotoluenesulphinic acid with methyl alcohol.

IV. When paramethoxyorthotoluenesulphonamide is oxidized by potassium permanganate, paramethoxybenzoic sulphinide is formed. From this can be obtained paramethoxyorthosulpho-benzoic acid.

V. Paramethoxyorthosulphobenzoic acid is isomeric with sulphanisic acid, and, when fused with potassium hydroxide, it gives resorcin and β-resorcylic acid are formed.

ON THE EXISTENCE OF DOUBLE SALTS IN SOLUTION.

By C. E. Linebarger.

If a solution of two salts be concentrated, they will pass from the dissolved into the solid state in one of four ways: (1) The salts may assume independently the solid state. If their solubilities be considerably different, one may pass almost completely out of solution before the other even commences to do so. Upon this fact is based the process of separation known as "fractional crys-

tallization." (2) The two salts may assume simultaneously the solid state, forming an isomorphous mixture. Two cases are to be distinguished: (*a*) the mixed crystals are miscible in all proportions; (*b*) one or the other of the component crystals is in excess. There may be a limited or an unlimited capability of mixture, just as liquids may be miscible in all proportions, as alcohol and water, or in limited proportions, as water and ether. (3) The crystals may separate out of the solution in definite stoichiometrical proportions. The crystalline compound may be a complex or a double salt, the criterion of a double salt being that it gives in aqueous solution the same reactions as its components. (4) The salts may form mixed crystals as well as double salts, but only within certain limits of concentration.

It is a debated question whether double salts exist as such in solution, or first come into being at the moment of crystallization. Yet much work has been done upon the subject, and from various points of view. Especially have experiments upon diffusion been performed, for the purpose of getting information as to the state of dissolved double salts. Graham[1] found that the constituent salts of certain double salts, as alum and the like, were present in the diffusate in different proportions from those in the double salt, as they diffused with different velocities; a fact that indicates a partial decomposition, at least, of the double salts. On the other hand, his experiments with the double sulphates of copper and potash, and of magnesia and potash, led him to conclude that these double salts dissolve in water without decomposition. But, as Marignac remarks,[2] these last experiments are not conclusive, since it was ascertained merely that the weight of the diffused double salt was equal to the sum of the weights of the component salts when diffused separately, and not that the relative proportions of the constituents remained constant. This latter investigator states that his experiments on the diffusion of pairs of salts did not seem to indicate that there was any difference between the behavior of solutions containing salts which form solid double salts and that of solutions of salts incapable of combining with each other. Van der Wal[3] performed some experiments on the diffusion of various double salts which showed that they were decompounded in solution. Ingenhoes,[4] also, states that the double salts

[1] Phil. Mag. 1850, p. 1.
[2] Ann. chim. phys. [5] **3**, 546 (1874).
[3] Inaugural Dissertation. Leyden, 1869.
[4] Ber. d. chem. Ges. **12**, 1678 (1879).

investigated do not exist in solution, "for they diffuse like the separate salts." Rüdorff[1] concluded from diffusion-experiments that double salts, although generally dissociated when dissolved, yet, shortly before crystallization, come into being. Trevor,[2] however, on repeating with some modifications Rüdorff's experiments on the double sulphates of copper and potassium, found it probable that that double salt does not exist at all in solution.

The changes of volume that take place when solutions of salts are mixed have been interpreted so as to disprove the existence of double salts in solution. Kremers,[3] on mixing solutions of salts capable of forming a double salt, found the volume of the mixture to be approximately equal to the sum of the volumes of the component salt solutions before mixing, if these contained the salts in molecular proportions. He therefore assumed that the combination of the two single salts to form the double salt did not take place in solution. Similar conclusions based upon like experimental data were arrived at by Favre and Valson.[4]

Appeal has been made to thermochemistry for facts that may aid us in deciding whether double salts exist in solution or not. Every true chemical change being accompanied by some thermal manifestation, solutions of salts capable of forming a double salt should, when mixed, absorb or evolve heat, provided that the double salt is formed in the solution. Berthelot[5] found that heat was evolved on mixing solutions of the halogen salts of mercury and of the alkalies. A similar observation was made by Graham[6] in the case of solutions of the chlorides of mercury and ammonium. His experiments with some double sulphates, however, showed that no heat was evolved on mixing their solutions. Observations of a similar kind were made by Favre and Silbermann[7] as well as by Favre and Valson.[8]

Valuable information as to the condition of double salts in solution is to be got from the knowledge of the freezing-points and electrical conductivities of their solutions. Raoult[9] determined the lowering of the point of congelation of solutions of fourteen double salts. Of these, with the exception of such as are formed with evolution of heat, the freezing-points were lowered to a temperature corresponding to the sum of the lowerings of the freezing-points of

[1] Ber. d. chem. Ges. **21**, 4, 1882 (1888).
[2] Ztschr. phys. Chem. **7**, 468 (1891).
[3] Aun. der Phys. Pogg. **98**, 58 (1856).
[4] Compt. rend. **77**, 907 (1873).
[5] Ann. chim. phys. [5] **29**, 202 (1883).
[6] Phil. Mag. **24**, 401 (1844).
[7] *Loc. cit.*
[8] *Loc. cit.*
[9] Compt. rend. **99**, 914 (1884).

solutions of the constituent salts, which indicates that dissociation had taken place. The theory of solubility-effect teaches that in the case of two salts possessing a common ion, the addition of one to a saturated solution of the other occasions a precipitation, unless a double salt is formed. Le Blanc and Noyes,[1] in making an investigation of solutions of certain salts in which no precipitation was caused by the addition of one salt to a solution of the other, found that in fact double salts were formed in the solution. Kistiaskowsky,[2] in seeking experimental proof of the propriety of the distinction between complex and double salts, drawn by Ostwald,[3] ascertained that the double salts examined by means of the cryoscopic method were almost completely decomposed into their components. On the electrical conductivity of solutions of double salts, work has been done by Hittorf,[4] Grotrian,[5] Klein,[6] Kistiaskowsky,[7] Wershoven,[8] Bouty,[9] Le Blanc and Noyes,[10] and Chroustshoff and Pachkoff,[11] the general results of which indicate that in dilute solutions, double salts are considerably dissociated, while in concentrated solutions their dissociation is but slight; this is especially the case with such salts as contain a salt of mercury or of cadmium.

The study of double salts in dynamic equilibrium with their solutions is of importance for the question under consideration. The simultaneous solution of two salts has been the subject of numerous investigations, some of which have a bearing upon the question as to the possibility of the existence of double salts in solution. Mulder[12] found that when water is saturated with two salts, there is often a simple equivalent ratio between the dissolved salts, indicating the presence of a double salt in solution. Rüdorff,[13] observing that on adding to saturated solutions of double salts an excess of one of the components, a part of the other was deposited from the solution, criticizes the conclusions of Mulder and states that a formation of double salts in solution cannot be thought of. But Trevor[14] has proven Rüdorff's experiments to be incomplete, so that his conclusions cannot be said necessarily to follow. The thorough investigations of Roozeboom,[15] Meyerhoffer,[16] and

[1] Ztschr. phys. Chem. **6**, 398 (1890). [2] *Ibid.* **6**, 97 (1890). [3] *Ibid.* **3**, 600 (1889).
[4] Ann. der Phys. Pogg. **106**, 524 (1859). [5] Ann. der Phys. Wied. **18**, 177 (1883).
[6] *Ibid.* **27**, 151 (1886). [7] *Loc. cit.* [8] Ztschr. phys. Chem. **5**, 481 (1890).
[9] Ann. chim. phys. [6] **14**, 78 (1888). [10] *Loc. cit.* [11] Compt. rend. **108**, 1162 (1889).
[12] Jsb. Chem. **1864**, 92, and **1866**, 65. [13] Ann. der Phys. Pogg. **148**, 558 (1873).
[14] Ztschr. phys. Chem. **7**, 468 (1891). [15] *Ibid.* **2**, 513 (1888). [16] *Ibid.* **3**, 336 and **5**, 97.

Schreinemaker,[1] on the states of equilibrium of double salts with their solutions, show that the few double salts examined are capable of existence in concentrated solution within certain limits of concentration.

Bodländer[2] has shown, by means of determinations of the solubility of the molecular compound of ammonia and silver chloride, as well as of the freezing-points and electrical conductivity of its solutions, that it certainly exists in solution.

Fischer and Schmidner[3] determined the relative quantities of the components of double salts whose solutions had been drawn up by capillary attraction into rolls of filter-paper placed in a tube. Experiments carried out with double salts soluble in alcohol as well as in water, showed that while in aqueous solution a larger amount of the more diffusible component was taken up by the paper than of the less diffusible component, in alcoholic solution the ratio of the quantities of the components found in the paper was the same as that in the double salt. These facts show that water, but not alcohol, has the power of decompounding the double salts examined.

On comparing the results of the foregoing investigations we see that double salts, as regards their capability of existing in solution, may be divided into two groups. The first group embraces the double sulphates, the double halides of the alkalies and alkaline earths, and the like; the second group comprises the double halide salts of mercury or of cadmium with the alkalies. The members of the first group are almost completely decompounded in solution, as shown by experiments on the contractibility, diffusibility, electric conductivity and freezing-points of their solutions, as well as by the circumstance that no thermal change is manifested on mixing solutions of their component salts. One, at least, of the constituent salts crystallizes with water of crystallization, and both undergo electrical dissociation to a not inconsiderable degree. The members of the second group are but slightly decompounded in concentrated solutions, although on dilution they become more so. When solutions of their components are mixed, heat comes into play. Their freezing-points and electrical conductivities differ widely from the sums of those of their components. One, at least, of the simple salts does not crystallize with water of crystallization, and suffers merely a slight dissociation into its ions.

[1] Ztschr. phys. Chem. **9**, 57. [2] *Ibid.* **9**, 730. [3] Ann. Chem. (Liebig) **272**, 156 (1892).

All of the facts observed with regard to aqueous solutions of double salts can be satisfactorily accounted for by means of Arrhenius' electrochemical theory. The existence of double salts in solution depends upon the temperature and degree of dilution. Likewise the degree of electrical dissociation of salts depends upon the temperature and concentration. If solutions of salts which are almost completely dissociated into their ions be mixed, no evidence of a chemical action is apparent. This is also the case if the salts are capable of combining with each other to form a solid double salt. The undissociated portions of the salts may indeed unite to form the double salt, but the reaction is inappreciable, and the more so the greater the electrical dissociation. As the ions of the simple salts lead an independent existence in solution, no appreciable formation of a double salt occurs except in the moment of crystallization. The double salts of the first group correspond in a measure to these conditions. If, however, one of the constituents of a double salt suffer but a slight decomposition into its ions, it is found that solutions of the component salts, when mixed, give out heat, and that the physical properties of the solution vary with the concentration. Such phenomena are observed especially with solutions of double salts of the second group. As the "activity-coefficient" increases with dilution, the more dilute the solution the greater the proportion of electrically dissociated to undissociated molecules. The degree of dissociation into ions increases also with the temperature, so that for a given concentration there exists a temperature above which electrical dissociation is so nearly complete that no double salt can be said to exist. In answering, then, the question as to the existence of double salts in aqueous solution, we should first ascertain what is the state of the components at the given temperature and concentration. That known, we can compute what amount of double salt may be present as such in solution.

These considerations obtain only for aqueous solutions. The experiments of Fischer and Schmidner (*loc. cit.*) show that in alcohol, a liquid that exerts but little dissociative power, double salts are soluble without decomposition, at least at ordinary temperatures. It seemed desirable to extend such observations to other liquids and other double salts. I have accordingly made a study of solutions of certain double salts in several organic solvents, the results of which are given in this paper.

Of the pairs of salts examined, one of each pair was practically insoluble in the solvents employed. Solutions of the soluble salt were kept in contact with the insoluble salt at a constant temperature. The assumption made was that if any of the insoluble salt entered into solution, it would do so with formation of the double salt. Hence the quantities of the dissolved salts should be in stoichiometrical ratio, and, if that was found to be the case, the conclusion that the double salt exists as such in solution would be legitimate. The experiments were carried out as follows: An excess of the insoluble salt was added to a solution of the soluble salt, and the whole kept at a constant temperature, with frequent and thorough agitation. After 36–40 hours, samples of the solution were drawn off by means of a pipette, introduced into a small glass-stoppered flask, weighed, the solvent distilled off, and the residue analyzed.

Benzene, Mercuric Chloride and Sodium Chloride.

Benzene[1] was added to a large excess of mercuric[2] as well as of sodium[3] chloride, and the whole was digested at 40° for 48 hours. A portion of the solution was then removed and the benzene and corrosive sublimate determined.[4] Table I. records the results.

TABLE I.

Wt. of Sol.	Wt. of Benzene.	Wt. of Residue.	Wt. of $HgCl_2$.
13.473 grams.	13.361 grams.	0.112 gram.	0.1124 gram.

from which it is seen that no sodium chloride has entered into solution. The conclusion to be drawn is that any double salt of corrosive sublimate and common salt is incapable of existence in benzene solution.

Acetone,[5] Mercuric Chloride and Sodium Chloride.

Mercuric chloride reacts chemically upon acetone at ordinary temperatures, so that this system of substances does not admit of

[1] The benzene had been carefully freed from thiophene by treatment with sulphuric acid. It was then repeatedly crystallized, and finally distilled over sodium.

[2] This was the commercial *c. p.* article and had been purified by a couple of crystallizations from water.

[3] Commercial *c. p.* sodium chloride was dissolved in water and precipitated by passing hydrochloric acid gas into the solution. The salt was ignited in a platinum dish to remove the last traces of moisture.

[4] The mercuric chloride was determined volumetrically by means of a standard solution of potassium iodide. The method gave very concordant results.

[5] Obtained by repeated fractional distillations of commercial article. It boiled at 56.4° at 757 mm. pressure.

a very accurate study. Still I have carried out some experiments with not too concentrated solutions at low temperatures, the results of which are given in Table II.

TABLE II.

Temperatures,	0°	0°	0°	0°	0°	5°	10°
Molecules of $HgCl_2$ to 100 mols. of $(CH_3)_2CO$	12.0	22.0	8.6	5.1	4.4	2.6	21.0
Molecules of NaCl to 100 mols. of $(CH_3)_2CO$	11.2	22.9	8.3	4.9	4.4	2.7	21.1

It is seen that the ratio of the number of molecules of the two salts is as 1 : 1, that is, a double salt consisting of one molecule of mercuric chloride and one molecule of sodium chloride is formed. On allowing a saturated solution of the two salts to evaporate I obtained a double salt crystallizing in long needles, the composition of which is represented by the formula $(HgCl_2)_2NaCl$. The salt $HgCl_2.NaCl$ I have as yet been unable to obtain from acetone solution. This is probably due to the different solubilities of the two double salts.

Acetic Ether,[1] *Mercuric Chloride and Sodium Chloride.*

When sodium chloride is added to solutions of mercuric chloride in acetic ether, it dissolves rapidly and, if it be in excess, the resulting solution always contains one molecule of common salt to two molecules of corrosive sublimate. The results of a series of determinations are given in Table III.

TABLE III.

Temperatures,	30°	33°	41.8°	42°	45°	48°
Mols. of $HgCl_2$ to 100 mols. $C_4H_8O_2$,	21.1	24.5	2.5	34.0	8.0	17.1
Mols. of NaCl to 100 mols. $C_4H_8O_2$,	10.7	12.2	1.2	17.0	4.1	8.4

This table shows that in acetic-ether solution a double salt with the composition represented by the formula $(HgCl_2)_2.NaCl$ is formed. That only this double salt is present in the solution is proven by the following experiments: The double salt $HgCl_2.NaCl.2H_2O$ (prepared by dissolving equal numbers of molecules

[1] Carefully distilled fractionally over calcium chloride and finally over a little sodium. Boiling-point was 74.4° at 757 mm.

of the salts in water and recrystallizing from dilute alcohol) was carefully dehydrated at 100°, and a portion added to acetic ether. A precipitation of salt took place, and an analysis of the solution showed the two salts to be in the same proportions as in the double salt $(HgCl_2)_2.NaCl$, that is, a decomposition took place in accordance with the following equation:

$$2(HgCl_2.NaCl) = (HgCl_2)_2.NaCl + NaCl.$$

The results of a number of analyses of solutions obtained in this way are given in Table IV.

TABLE IV.

Temperatures,	15°	25°	30°	35°	40°
Mols. of $HgCl_2$ to 100 mols. $C_4H_8O_2$,	12.1	8.0	20.0	4.0	24.1
Mols. of NaCl to 100 mols. of $C_4H_8O_2$,	6.1	4.0	9.8	2.1	12.3

If sodium chloride dissolves in acetic-ether solution of mercuric chloride with formation of the double salt $(HgCl_2)_2.NaCl$, the number of dissolved molecules must remain unchanged. Now as the amount of the depression of the freezing-point as well as of the elevation of the boiling-point depends upon the number of dissolved molecules, the addition of common salt to a solution of corrosive sublimate in acetic ether ought not to alter the boiling- or freezing-point of that solution. This has been found to be true in the case of the boiling-point, a freezing-point determination naturally being impracticable with such a solvent as acetic ether. The temperature of a boiling solution of mercuric chloride in acetic ether was determined by means of the apparatus used in determining molecular weights, and, without the boiling being discontinued, small quantities of sodium chloride were added from time to time. It was impossible to detect any change in the boiling-point.

The preceding experiments show that the double salt $(HgCl_2)_2.NaCl$ exists in acetic ether solution at temperatures between 0° and 50°. At somewhat higher temperatures, however, the salt becomes decompounded. Thus, a solution of the double salt when heated to about 140° in a sealed tube deposits a portion of the salt.

Acetic Ether, Mercuric Chloride and Potassium Chloride.

Small quantities of potassium chloride were added from time to time to a saturated solution of mercuric chloride, the temperature being kept at 40°, and after equilibrium had established itself, a sample of the solution was removed and analyzed. Soon, however, a white flocky precipitate separated out, which had a composition corresponding to the formula $HgCl_2.KCl$. This double salt was also obtained by adding all at once one molecule of finely powdered potassium chloride to one molecule of mercuric chloride dissolved in considerably more acetic ether than necessary for saturation. After a few days nearly all the corrosive sublimate had been precipitated from solution. No double salt of these two salts seems capable of existence in acetic ether solution.

Acetic Ether, Mercuric Chloride and Lithium Chloride.

In Table V. are given the results of some determinations of the solubility of lithium chloride in solutions of mercuric chloride in acetic ether.

TABLE V.

Temperatures,	0°	10°	20°	30°	40°
Mols. $HgCl_2$ to 100 mols. $C_4H_8O_2$,	8.2	0.9	6.3	0.6	6.4
Mols. LiCl to 100 mols. $C_4H_8O_2$,	8.5	1.0	6.5	0.9	6.8

Here it is permitted to assume that the double salt $HgCl_2.LiCl$ is formed, the excess of lithium chloride over one molecule being due to its slight solubility.

Experiments of a qualitative nature were carried out with solutions of cadmium bromide and cadmium iodide in acetone as well as in acetic ether. It was found that the chlorides of potassium and sodium were quite freely soluble in such solutions, undoubtedly with formation of double salts.

A consideration of the foregoing experiments shows that the temperature and the nature of the solvent are of decided influence in determining the kind and stability of the double salts that may be formed in it. But little influence can be ascribed to the degree of dilution in the case of solvents which do not have any considerable electric dissociative power, although in aqueous solutions the concentration plays an important part. The number of double

salts studied above might be extended indefinitely. Of the greatest importance, however, would be the study of one system throughout a considerable range of temperature; accordingly, I am engaged in the investigation of the states of equilibrium of the system composed of the substances acetic ether, mercuric chloride and common salt, which seems admirably adapted for such work.

CHICAGO, ILL., *March* 22, 1893.

Contributions from the Chemical Laboratory of Cornell University.

THE MOLECULAR WEIGHT OF HYDROGEN PEROXIDE AND OF BENZOYL PEROXIDE.

BY W. R. ORNDORFF AND JOHN WHITE.

Although hydrogen peroxide, because of its peculiar nature and its various applications in the arts and sciences, has been the subject of much study, it is only very recently that any attempt has been made to determine its molecular weight. This has without doubt been chiefly due to the ease with which the substance decomposes and the difficulty of obtaining perfectly pure solutions, also because, until the development of Raoult's Law and its application by Beckmann, no method was known by which its molecular weight could be determined.

Early investigators proved by analytical means that hydrogen peroxide contains double the amount of oxygen found in water, and expressed this by using the simplest formula in accordance with the facts: HO_2, or, with the present system of atomic weights, H_2O_2.

Tammann,[1] making use of the cryoscopic method of determining molecular weights, obtained results which led him to the conclusion that the formula for hydrogen peroxide is double that usually employed, *i. e.*, H_4O_4 instead of H_2O_2.

Such a conclusion would in itself be sufficiently startling, involving as it does a theory of linkage of the atoms in which oxygen

[1] Ztschr. phys. Chem. **4**, 441.

is trivalent; but if in addition to this there be taken into consideration the peculiar nature of his experimental data and the methods by which the conclusion was deduced, it becomes apparent that the work needs confirmation. The authors of this paper, therefore, undertook a repetition of Tammann's work, and had already obtained results leading to a conclusion different from that deduced by him, when an article on the same subject by Carrara[1] appeared. Carrara made determinations of the molecular weight of hydrogen peroxide in aqueous solution, using the cryoscopic method, and also determined the coefficient of refraction of solutions of the substance. In both cases he obtained results which led to the conclusion that the correct formula for hydrogen peroxide is H_2O_2.

We have, then, two conclusions as to the molecular weight of hydrogen peroxide, both deduced from results obtained from the lowering of the freezing-point of its aqueous solution, one giving as its formula H_4O_4, the other H_2O_2. It may be stated here that the results of the authors' work, most of which was done before they had seen Carrara's article, lead to the same conclusion as that deduced by him, *viz.*, that the formula for hydrogen peroxide is H_2O_2.

In establishing this conclusion, they have determined not only the molecular weight of hydrogen peroxide, but also that of the most stable of the organic derivatives of hydrogen peroxide, *i. e.*, benzoyl peroxide, $(C_6H_5CO)_2O_2$, described by Brodie.[2]

Experimental.

Preparation of a pure solution of hydrogen peroxide.—For the purpose of obtaining a pure solution of hydrogen peroxide, the commercial solution, labeled pure and for medicinal purposes, was used as a starting-point, and the methods of purification were essentially those given by Hanriot.[3]

This solution was found to contain small amounts of the following substances: barium, calcium, sodium, aluminium, iron; hydrochloric, sulphuric and phosphoric acids; also a small amount of an insoluble substance which was found to consist chiefly of silica. To purify this solution a concentrated solution of barium hydroxide was added until it gave an alkaline reaction, this precipitated all

[1] Gazz. chim. ital. (1892), **10**, 1.

[2] Proc. Roy. Soc. **9**, 361; **12**, 655; Phil. Mag. [4] **17**, 301; **27**, 469; also Phil. Trans. (Lond.) (1863), 153, 407; Q. J. Chem. Soc. **17**, 266.

[3] Compt. rend. **100**, 57, 172.

sulphates, phosphates, and any iron and aluminium present; the solution was then filtered and the barium exactly precipitated by dilute sulphuric acid, and then a small quantity of phosphoric acid was added. After the precipitate had settled, the solution was again filtered and subjected to distillation under reduced pressure. The following apparatus was used for this purpose: a large distilling-flask (about 1 l.), with a contraction in the neck near the bulb for the purpose of filling the neck with glass beads; the flask was closed with a two-hole rubber stopper, through one hole of which a thermometer was passed, and through the other a long piece of small capillary tubing, the lower end of which reached to within a few centimeters of the bottom of the flask. This tube was closed at its upper end by means of a piece of rubber tubing provided with a Hofmann screw clamp; this was for the purpose of regulating the current of air which was passed through the solution, thus preventing the violent bumping which ensues if this precaution be not taken. The distilling-flask was connected by air-tight joints with a condenser and receiver. The exhaustion was produced by means of a powerful water-pump, and the pressure was reduced to 2.5–3 centimeters of mercury. After one-third of the liquid had been distilled off, the distillate was found to contain very little hydrogen peroxide, but a small quantity of hydrochloric acid; another third contained more of the hydrogen peroxide, but still a comparatively small quantity. The beads were then removed from the neck of the flask, and the distillation continued until decomposition began. A small quantity of water was then added and the distillation continued until only a small quantity of liquid remained. The third distillate was found to consist entirely of a moderately concentrated solution of pure hydrogen peroxide, which was further concentrated by freezing out the water and pouring off the liquid remaining. A considerable quantity of this solution, evaporated to dryness, left only the faintest trace of a residue, and tests made showed the entire absence of any of the impurities previously found to be present. The solution itself was found, by using very delicate litmus paper, to be very slightly acid; this is in accord with the statement made by Hanriot. This solution undergoes no decomposition if kept cold.

For the purpose of determining the molecular weight of hydrogen peroxide, use was made of the apparatus and thermometer

devised and described by Beckmann[1] for the determination of freezing-points of solutions. A glass stirrer was used, and bits of broken glass with sharp edges were put into the apparatus to furnish a starting-point for the formation of ice. Platinum, as is well known, cannot be used, since it acts catalytically, inducing decomposition of the hydrogen peroxide.

Method of Work.—After determining the weight of the empty tube, pure distilled water was introduced by means of a pipette, and the freezing-point noted, several successive determinations being made to insure constancy in the readings. The solution of hydrogen peroxide was then introduced by means of a pipette, the total weight determined to centigrams, and the freezing-point again taken, thus giving the depression due to the hydrogen peroxide (successive determinations made with the same solution showed no change in the readings). The solution was then poured into a beaker, the apparatus washed by successive additions of pure water, the contents of the beaker largely diluted with water, acidulated with sulphuric acid, and the amount of hydrogen peroxide determined by titrating with a very dilute solution of potassium permanganate of known strength. The weight of hydrogen peroxide found subtracted from the total weight of the solution gives the weight of the solvent. The concentration could be changed at will by pipetting into the apparatus water and hydrogen peroxide solution in varying amounts.

The results obtained were in each case satisfactory, the deviations from the calculated values being such as from the nature of the experiment one would expect. The tabulated results follow:

Hydrogen Peroxide, $H_2O_2 = 34$.

Solvent, WATER; molecular depression, 19; depression-coefficient, 0.558.[2]

Wt. Solv.	Wt. Sub.	Concent.	Depress.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
16.48	0.0207	0.1256	0.069	0.549	18.7	34.6
18.84	0.0509	0.2705	0.151	0.558	19.0	34.0
20.84	0.0761	0.3653	0.216	0.591	20.1	32.1
21.90	0.0943	0.4306	0.246	0.571	19.4	33.3
23.61	0.1211	0.5130	0.288	0.561	19.1	33.9

[1] Ztschr. phys. Chem. 2, 638.

[2] The results given in this table are exactly as they were found. No determination has been omitted.

Wt. Solv.	Wt. Sub.	Concent.	Depress.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
37.30	0.2279	0.6110	0.354	0.579	19.7	32.8
29.78	0.1949	0.6544	0.380	0.580	19.7	32.7
19.93	0.1451	0.7280	0.434	0.596	20.3	31.8
17.79	0.1834	1.0310	0.571	0.554	18.8	34.3
19.86	0.2735	1.3773	0.746	0.541	18.4	35.0
17.84	0.2634	1.4767	0.805	0.545	18.5	34.8

For the sake of comparison the tabulated results obtained by Carrara and by Tammann are here given:

Carrara:—Molecular Weight of Hydrogen Peroxide.

Concentration.	Depression.	Dep.-coef.	Molec. Dep.	Mol. Wt. found.[1]
0.199	0.120	0.603	20.5	31.5
0.337	0.200	0.593	20.2	32.0
0.382	0.235	0.615	20.9	30.9
0.452	0.265	0.586	19.9	32.4
0.659	0.390	0.591	20.1	32.1
0.662	0.400	0.604	20.5	31.5
0.876	0.500	0.570	19.4	33.3
1.139	0.650	0.570	19 4	33.3
1.554	0.905	0.582	19.8	32.6
2.338	1.350	0.577	19.6	32.9
3.240	1.840	0.567	19.3	33.4
3.295	1.880	0.570	19.4	33.3

Tammann:—Molecular Weight of Hydrogen Peroxide.

Concentration.	Depression.	Dep.-coef.	Molec. Dep.[1]	Mol. Wt. found.[2]
0.295	0.109	0.369	12.6	51.4
0.367	0.152	0.414	14.1	45.8
0.457	0.200	0.437	14 9	43.4
0.568	0.279	0.491	16.7	38.6
0.705	0.367	0.520	17.7	36.4
0.873	0.472	0.541	18.4	35.1
1.080	0.609	0.563	19.1	33.6
1.331	0.785	0.589	20.0	32.2

Several points of interest are brought out by a comparison of these tables. First, it will be seen that there is a striking similarity

[1] Calculated by the authors from the data given by Carrara.
[2] Calculated by the authors from the data given by Tammann.

between the results obtained by Carrara and those obtained independently by us, the deviation from the calculated values for the molecular depression and for the depression-coefficient being slight in both cases, and not more than can be explained by the deviations ordinarily to be expected in such determinations. These deviations are somewhat less in our results than in those of Carrara, which may be explained upon the assumption that the solution of hydrogen peroxide used by us was purer than that used by him; or possibly it may be owing to slight errors in his determinations of the freezing-points, since he does not seem to have read the thermometer usually beyond the hundredths of a degree, whereas it is possible to obtain readings correct to within one thousandth of a degree by means of a good lens.

It is impossible to reconcile the results obtained by Tammann with those obtained by Carrara and by us. They are, as Carrara also points out, exceedingly peculiar, in that with increasing dilution there is a corresponding decrease in the depression-coefficient and an increase in the molecular weight found, whereas the opposite has almost invariably been found to be the case.[1] It is interesting to note what values for the molecular weight would, upon this supposition, have been obtained had the dilution been carried still further.

It seems to us that the only explanation which can be offered for this peculiar behavior of Tammann's solutions is that, assuming he had a pure solution of hydrogen peroxide, he used a platinum stirrer and probably platinum clippings, such as are commonly used in the apparatus to facilitate the formation of ice. The platinum, acting catalytically upon the hydrogen peroxide, would cause decomposition, and such decomposition would naturally produce in the final results a greater proportionate error the more dilute the solution. His use of interpolation-formulas in a case where there is such a wide difference in the results obtained is scarcely justifiable.

The Molecular Weight of Benzoyl Peroxide.

Of the various derivatives of hydrogen peroxide which have been described, we selected benzoyl peroxide as the one best suited for our purpose, because of the ease with which it is prepared in pure condition and because of its comparative stability.

[1] *Cf.* Beckmann's results, Ztschr. phys. Chem. **2**, 715; **7**, 323.

Preparation of Benzoyl Peroxide.—Benzoyl peroxide was prepared by the method given by Brodie. Benzoyl chloride, free from phosphorus oxychloride, was mixed in a vessel with a small quantity of water,[1] a little less[2] than the equivalent amount of pure barium peroxide hydrate, $BaO_2.8H_2O$, was added, and the whole stirred to a thin paste; action began within a few minutes, accompanied by a slight elevation of temperature, and was completed in the course of eight to ten hours. The benzoyl peroxide, mixed with some benzoic acid and barium chloride, was obtained as a solid hard mass. This was pulverized, washed with water until free from barium chloride, then treated with a dilute solution of sodium carbonate to remove the benzoic acid, and again washed with water until it no longer had an alkaline reaction. The white, powdered benzoyl peroxide was dried over sulphuric acid in a vacuum and the dried substance recrystallized from boiling ether. After two or three crystallizations the substance was obtained in pure state, in beautiful transparent orthorhombic crystals[3] with a melting-point of 103° C. (uncor.). Brodie gives the melting-point as 103.5° C.

The molecular weight of benzoyl peroxide was determined by the freezing-point, as well as by the boiling-point, method described by Beckmann.[4] Two solvents were used in each case, benzene and glacial acetic acid for the freezing-point determinations, and ether and chloroform for the boiling-point determinations. Benzene was found to be the best solvent for the freezing-point determinations, since benzoyl peroxide is not very soluble in glacial acetic acid. In working with glacial acetic acid some difficulty was experienced, at first, owing to the absorption of moisture by the solvent during the experiment. This was obviated by passing the platinum stirrer through a small glass tube, fitted tightly into the cork, alongside of the thermometer. The upper end of this glass tube was connected with the stirrer by a small, thin rubber bag. This allowed free play of the stirrer up and down through the tube, but excluded both air and moisture.

[1] Monatsh. Chem. **7**, 522; Lippmann and Sonnenschein found that the yield was increased by the use of a little water.

[2] It is best to have a slight excess of benzoyl chloride, as barium peroxide decomposes benzoyl peroxide.

[3] An examination of these crystals kindly made for us by Mr. A. S. Eakle of the Geological Department of this University showed the faces ∞ P $\bar{\infty}$, ∞ P $\breve{\infty}$, P $\breve{\infty}$, ∞ P, 3 P, P$\bar{\infty}$. *Cf.* Miller: Proc. Roy. Soc. **12**, 394.

[4] Ztschr. phys. Chem. **2**, 638; **7**, 323; **4**, 543; **6**, 437; **8**, 223.

Chloroform was found to be the best solvent for the boiling-point determinations, because, its boiling-point being higher than that of ether, it was easier to regulate the temperature—an important point in the use of this method—and, moreover, benzoyl peroxide is much more soluble in chloroform than in ether. In both methods the weighed substance was introduced into the apparatus by means of the side tube provided for the purpose, in the form of a compressed tablet.

The results of the freezing-point determinations follow:

Benzoyl Peroxide, $(C_6H_5CO)_2O_2 = 242$.

Solvent, BENZENE; molecular depression, 49; depression-coefficient, 0.2023.

Crystallized from acetone—

Wt. Solv.	Wt. Sub.	Concent.	Depres.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
15.62	0.0954	0.6108	0.132	0.2161	52.3	227
	0.2318	1.4840	0.320	0.2156	52.2	227
	0.3998	2.5595	0.544	0.2125	51.4	230
	0.5819	3.7253	0.791	0.2123	51.4	231
	0.7654	4.9000	1.020	0.2084	50.4	235
15.42	0.1472	0.9546	0.199	0.2084	50.4	235
	0.3747	2.4299	0.496	0.2041	49.2	240
	0.5587	3.6230	0.736	0.2031	49.2	241

Crystallized from ether—

15.00	0.1209	0.8060	0.173	0.2146	51.9	228
	0.2483	1.6553	0.348	0.2103	50.9	230
	0.4055	2.7033	0.568	0.2101	50.8	233
	0.5856	3.9040	0.809	0.2072	50.1	236
	0.7933	5.2887	1.089	0.2059	49.8	238
15.00[1]	0.2932	1.9547	0.400	0.2046	49.5	239
	0.6096	4.0640	0.822	0.2023	48.9	242
	0.9810	6.5400	1.311	0.2005	48.5	244

Crystallized from benzene—

13.71	0.1427	1.0408	0.219	0.2104	50.9	233
	0.3320	2.4216	0.503	0.2077	50.2	236
	0.5236	3.8191	0.787	0.2061	49.9	238

[1] This set of determinations was made with a freshly prepared sample of benzoyl peroxide, which was recrystallized from ether four times.

Solvent, ACETIC ACID; molecular depression, 39; depression-coefficient, 0.1611.

Crystallized from ether—

Wt. Solv.	Wt. Sub.	Concent.	Depres.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
16.79	0.1509	0.8982	0.152	0.1692	40.9	230
	0.2954	1.7583	0.294	0.1672	40.4	233
	0.4669	2.7791	0.453	0.1630	39.4	239
19.86[1]	0.2068	1.0413	0.167	0.1604	38.8	243
	0.4218	2.1239	0.331	0.1558	37.7	250
	0.6594	3.3202	0.508	0.1530	37.0	255

The results of the boiling-point determinations are as follows:

Benzoyl Peroxide, $(C_6H_5CO)_2O_2 = 242$.

Solvent, ETHER; molecular rise for 100 grams, 21.1°; barometer constant.

Crystallized from ether—

Wt. Solv.	Wt. Sub.	Concent.	Rise.	Mol. Rise.	Mol. Wt. found.
48.79	0.2974	0.6094	0.054	21.3	238
	0.5812	1.1912	0.110	22.3	229
42.50	0.3533	0.8313	0.079	23.0	222
	0.6571	1.5461	0.134	21.0	243
	0.9819	2.3103	0.208	21.8	234
	1.2873	3.0290	0.268	21.4	238
24.72[2]	0.4187	1.6938	0.148	21.2	241
23.94	0.6491	2.7114	0.236	21.1	242
25.34	0.4800	1.8942	0.156	19.9	256
	0.8325	3.2853	0.271	19.9	256

Solvent, CHLOROFORM; molecular rise for 100 grams, 36.6°; bar. 742.5–741.5 mm.

Crystallized from ether—

Wt. Solv.	Wt. Sub.	Concent.	Rise.	Mol. Rise.	Mol. Wt. found.
98.18	0.3945	0.4018	0.063	37.9	233
	0.7573	0.7713	0.120	37.6	235
	1.0459	1.0653	0.160	36.3	244
	1.3295	1.3541	0.196	35.0	253
	1.6303	1.6603	0.234	34.1	260
	1.8820	1.9168	0.270	34.1	260

[1] This set of determinations was made on a freshly prepared sample of benzoyl peroxide which had been recrystallized from ether four times.

[2] These determinations were kindly made for the authors by Mr. B. H. Hite of the Johns Hopkins University.

An attempt was also made to determine the molecular weight of benzoyl peroxide in solution in benzene by the boiling-point method, but it was found that, at the boiling-point of benzene, benzoyl peroxide undergoes partial decomposition.[1] The solution becomes colored and acquires a peculiar odor. Some of the benzoyl peroxide recovered from this solution by allowing the benzene to evaporate spontaneously was found to have a very peculiar odor, and when recrystallized from ether melted at 97°–98°. This low melting-point was probably due to the presence of phenyl benzoate or of diphenyl, products of the decomposition of benzoyl peroxide.

Summary.

1. The results obtained by Carrara, as well as those obtained by us, from the depression of the freezing-point of aqueous solutions of hydrogen peroxide, show that the formula of the substance is H_2O_2, as the molecular weight is not far from 34. This conclusion differs from that deduced by Tammann, but it is probably more correct, being based on more accurate data.

2. The results obtained from the depression of the freezing-point of solutions of benzoyl peroxide show the molecular weight of this substance to be about 242; its formula must be, therefore, $(C_6H_5CO)_2O_2$, and consequently that of hydrogen peroxide must be H_2O_2.

3. The results obtained from the rise of the boiling-point of solutions of benzoyl peroxide lead to the same conclusion as that stated in 2., *viz.*, that the molecular weight of benzoyl peroxide is about 242 and its formula $(C_6H_5CO)_2O_2$, and consequently the formula of hydrogen peroxide is H_2O_2.

These results are also in accord with the results obtained by Carrara from determinations of the coefficients of refraction of solutions of hydrogen peroxide.

Cornell University, *April*, 1893.

[1] This is contrary to the statement made by Lippmann that in the cold or at the boiling-point of benzene, benzoyl peroxide undergoes no change.

MIXED DOUBLE HALIDES OF LEAD AND POTASSIUM.

Supplementary Note.

By Charles H. Herty.

While the investigation of mixed double halides of lead and potassium[1] was in progress, the existence of only one bromoplumbite of potassium, $KPbBr_3.H_2O$,[2] was known; consequently, after finding so many of the compounds obtained in that investigation to be mixtures of the simple double salts $KPbI_3.xH_2O$ and $KPbBr_2.xH_2O$, it was deemed unnecessary to make quantitative analyses of the compounds *C*, *D* and *E* in the section "Compounds formed from Solutions containing Decreasing Quantities of Iodine and Increasing Quantities of Bromine." Only qualitative tests were made whereby the presence of iodine and bromine was shown in all of the compounds.

Recently[3] Wells has shown the existence of three other bromoplumbites of potassium, $K_2PbBr_4.H_2O$, $3KPbBr_3.H_2O$, and KPb_2Br_5. It has seemed advisable, therefore, to determine the composition of mixtures in which the bromoplumbite is largely in excess of the iodoplumbite. To this effect the following series of compounds have been prepared and analyzed. Six portions of potassium bromide, 27.35 grams each, were dissolved each in 40.95 grams of water. To one portion was added 3 grams of lead iodide and 4.7781 grams of lead bromide. The mass was then boiled in a flask attached to an inverted condenser until solution was effected. From this solution, on cooling, bundles of lath-shaped crystals separated. These were dried and labeled *A*. Similarly, to a second portion was added 2 grams of lead iodide and 5.5745 grams of lead bromide. Bundles of lath-shaped crystals were again obtained. These were labeled *B*. To a third portion was added 1.50 grams of lead iodide and 5.9727 grams of lead bromide. Lath-shaped crystals were again obtained, but the crystal form was very imperfect. These were labeled *C*. Qualitative tests showed the presence of a large quantity of bromine, but only a slight quantity of iodine, in this compound. To a

[1] This Journal **15**, 81. [2] *Ibid.* **14**, 124. [3] Amer. Jour. of Science **45**, 121.

fourth portion was added 0.5 gram of lead iodide and 6.7691 grams of lead bromide. Crystals similar to *C*, but in larger quantity, were obtained. Qualitative tests showed only the slightest trace of iodine. These were labeled *D*. To a fifth portion was added 0.1 gram of lead iodide and 7.0877 grams of lead bromide. Crystals similar to *C* and *D*, but in still larger quantity, were obtained. Qualitative tests showed the presence of bromine alone. These were labeled *E*. Finally, to determine the composition of the salt formed from a solution containing no iodine, there was added to the sixth portion of the potassium bromide solution 7.1676 grams of lead bromide. Crystals similar to *C*, *D* and *E* were obtained in abundance. These were labeled *F*. In the mass of these crystals were noticed several beautiful prismatic crystals, evidently different from the surrounding crystals. These were separated and labeled *G*.

Analyses of Compounds.

1.0011 grams *A* gave 0.0342 gram H_2O; 0.5743 gram $PbSO_4$ = 0.3922 gram Pb; 0.4922 gram K_2PtCl_6 = 0.0793 gram K; 1.1167 grams AgI and AgBr. This last was transformed into 0.8327 gram AgCl, which gives in original substance 0.0688 gram I and 0.4211 gram Br.

1.0012 grams *B* gave 0.0342 gram H_2O; 0.5812 gram $PbSO_4$ = 0.3969 gram Pb; 0.5017 gram K_2PtCl_6 = 0.0808 gram K; 1.1171 grams AgI and AgBr. This last was transformed into 0.8424 gram AgCl, which gives in original substance 0.0358 gram I and 0.4472 gram Br.

1.0016 grams *C* gave 0.0235 gram H_2O; 0.4985 gram $PbSO_4$ = 0.3404 gram Pb; 0.7594 gram K_2PtCl_6 = 0.1223 gram K; 1.1988 grams AgBr = 0.5102 gram Br. The quantity of iodine present in this compound as shown by the qualitative tests is so small that it cannot be accurately determined by conversion of the silver bromide and silver iodide into silver chloride.

1.0010 grams *D* gave 0.0230 gram H_2O; 0.5061 gram $PbSO_4$ = 0.3456 gram Pb; 1.1986 grams AgBr = 0.5101 gram Br; 0.7513 gram K_2PtCl_6 = 0.1210 gram K.

1.0012 grams *E* gave 0.0235 gram H_2O; 0.5068 gram $PbSO_4$ = 0.3461 gram Pb; 1.1983 grams AgBr = 0.5100 gram Br; 0.7503 gram K_2PtCl_6 = 0.1209 gram K.

1.0014 grams *F* gave 0.0217 gram H_2O; 0.5096 gram $PbSO_4$

$=0.3480$ gram Pb; 1.1963 grams $AgBr=0.5091$ gram Br; 0.7431 gram $K_2PtCl_6=0.1197$ gram K.

0.7202 gram *G* gave 0.0242 gram H_2O; 0.4255 gram $PbSO_4$ $=0.2906$ gram Pb; 0.8087 gram $AgBr=0.3442$ gram Br; 0.3676 gram $K_2PtCl_6=0.0592$ gram K.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	3.42	39.18	6.87	42.06	7.92	99.45
B	3.42	39.64	3.58	44.67	8.07	99.38
C	2.35	33.99	Trace	50.94	12.21	99.49
D	2.30	34.53	Trace	50.96	12.09	99.88
E	2.35	34.57	...	50.94	12.08	99.94
F	2.17	34.75	...	50.84	11.95	99.71
G	3.36	40.35	...	47.79	8.22	99.72

Practically all of the water of crystallization was driven off from these salts at 110°. *A* lost only 0.2 milligram more in weight on raising the temperature of the oven to 200° for two hours, than was lost at 110°; *E* lost only 1.5 milligrams more.

From the figures in the above table it is seen that so long as the iodoplumbite is present in any appreciable quantity the bromoplumbite is in the form of the salt $KPbBr_3.H_2O$. When, however, only a trace of iodine is present in the compound the bromoplumbite has the formula $K_2PbBr_4.H_2O$, the theoretical composition of this salt being H_2O, 2.89; Pb, 33.21; Br, 51.35; and K, 12.55 per cent.

The salt *G*, which was found crystallizing in the mass of *F*, is the salt $KPbBr_3.H_2O$, the theoretical composition of this salt being H_2O, 3.57; Pb, 41.06; Br, 47.61; and K, 7.76 per cent.

The fact that no salt corresponding to the formula $K_2PbBr_4.H_2O$ was obtained in the earlier work upon potassium bromoplumbite[1] is easily explained if the method of preparation used be compared with that used by Wells in the preparation of this salt.[2] It was obtained only when lead bromide was dissolved in very concentrated solutions of potassium bromide. This condition was never met with in my first experiments, for, in them, a solution of lead nitrate was added to a solution of potassium bromide until the precipitated lead bromide no longer dissolved; this precipitation of lead bromide necessarily left a solution much poorer in potassium bromide.

UNIVERSITY OF GEORGIA, *March* 17, 1893.

[1] This Journal **14**, 124.

[2] Amer. Jour. of Science **45**, 132.

A MODIFICATION OF THE STANNOUS-CHLORIDE METHOD FOR IRON TITRATIONS.

By R. W. Mahon.

Of the methods which have been proposed for determining iron in its ores, only those depending on titration with permanganate, bichromate, or stannous chloride have come into extensive use. Marguerite's method undoubtedly possesses certain advantages, but the objections to it have caused it to be abandoned by many of those who are engaged daily with iron estimations—among others the writer.

The method proposed so long ago as 1855 by Kessler, and since referred to by him with some minuteness,[1] is an adaptation of the bichromate titration, used extensively, which may be described briefly as follows: reduction of ferric chloride by stannous chloride in excess, and removal of the excess of stannous chloride, after dilution, by mercuric chloride in excess, followed without filtration, by titration with potassium bichromate. This method is accurate and easy of execution. Like all the bichromate titrations, it is, however, dependent upon the testing of drops taken from the solution, with potassium ferricyanide—a tedious operation.

Seeking for a rapid and accurate method of iron-estimation, and one easy of execution, I have observed that ferrous chloride has less affinity for chlorine than mercurous chloride has for chlorine: especially at or near the boiling-heat, and in solutions strongly acid with hydrochloric acid. If, therefore, to a solution of ferric chloride, near the boiling-temperature, containing free hydrochloric acid, and mercuric chloride, a solution of stannous chloride is added, the mercurous chloride, at first formed, redissolves, until all of the iron is reduced to the ferrous condition. A further addition of stannous chloride precipitates mercurous chloride.

In strongly acid solution a considerable excess of stannous chloride is necessary to cause this precipitation. The relation between ferric, mercuric, and stannous chlorides is the same as the relation between ferric, platinic, and stannous chlorides. At or near the boiling-heat, stannous chloride reduces all the iron, in

[1] Zischr. anal. Chem. **11**, 249.

solution strongly acid with hydrochloric acid, before reducing platinic chloride. The first drop of stannous chloride in excess reduces platinic to platinous chloride, which is not, however, apparent here, as it remains dissolved in the colorless fluid. If the addition of stannous chloride be continued, the formation of platinous chloride proceeds, and imparts a brownish red color to the solution. If mercuric and platinic chlorides are added to a solution of ferric chloride, strongly acid with hydrochloric acid, at or near the boiling-point, stannous chloride reduces all the iron first, and the first drops in excess cause the formation of a faint cloud of mercurous chloride, darkened and rendered instantly perceptible by finely divided mercury and platinum which are precipitated at the same time. A very minute trace of platinic chloride present in solution is sufficient to bring about this reaction.

This mixture, then, of mercuric and platinic chlorides is an indicator which can be used to advantage in titrations of iron by stannous chloride. In the frequent standardizations of stannous chloride with a standard solution of ferric chloride, which are necessary, it is desirable to employ approximately the same conditions of dilution and acidity, as well as approximately the same quantity of iron, as in the estimations. A correction, as in all titrations dependent on the production of tint imparted to a solution of definite bulk, is to be made. 0.2 cc. of stannous chloride of the strength used imparts a tint to 175 or 200 cc. of solution, which is easily remembered and reproduced. The indicator can be made from a solution of platinic chloride and a solution of mercuric chloride, to contain in one litre, metallic platinum 0.05 gram, and mercuric chloride 34.0 grams. Of such a solution 15 cc. is a suitable quantity to be used in each estimation.

The standard solution of ferric chloride is advantageously made of such strength that 1 cc. contains 0.01 gram of iron; the stannous chloride of approximately the same strength. Some arrangement for preserving the stannous chloride, and introducing it into the burette without unnecessary contact with the air, is necessary, such as that figured on page 409 of the 2d vol. of Fresenius, sixth ed. The burette should be of 100 cc. capacity. A suitable vessel for carrying out the titration is a 600-cc. Erlenmeyer flask.

The estimation of iron in its ores is performed as follows: Weigh accurately about 1 gram of ore into a 250-cc. beaker.

Cover with a watch-glass and digest in 20 cc. of hydrochloric acid, of 1.20 sp. gr., until decomposed. Add now 0.3 gram of potassium chlorate and digest a few moments longer. The glass and the rim of the beaker being washed down into the solution, which should now be about 40 cc. in volume, it is filtered and washed into an Erlenmeyer flask; 20 to 30 cc. of hydrochloric acid of 1.20 sp. gr., and 15 cc. of the indicator-solution are added. It is now ready for titration. Heat the covered solution to boiling. The trace of chlorine remaining escapes. Lower the light, and titrate at incipient boiling. The residue is prepared for titration by fusing with sodium carbonate, extracting with water and acid, and adding 15 cc. of the indicator. The iron in six ores was determined by the bichromate method (Kessler's), and by the stannous-chloride method with the indicator, with the following results:

$K_2Cr_2O_7$.	$SnCl_2$.
58.67	58.71
39.76	39.61
49.45	49.41
62.49	62.33
55.22	55.11
59.18	59.29

In one ore the iron was determined by three methods, with these results:

$KMnO_4$.	$K_2Cr_2O_7$.	$SnCl_2$.
57.30	57.26	57.33

I have made a large number of titrations by this method, to determine the best conditions of volume, acidity, temperature, and quantities of mercury and platinum to be used, and find them to be as above described.

To recapitulate: the volume of the solution before adding the stannous chloride being about 125 cc., should contain 20 to 40 cc. of hydrochloric acid, sp. gr. 1.20. This should be titrated at or just below incipient boiling, in the presence of a considerable quantity of mercuric chloride and only a trace of platinic chloride.

SPARROW'S POINT, MARYLAND, *April*, 1893.

REVIEWS AND REPORTS.

Recent Progress in Physical Chemistry, III.[1]

Zur Kinetik der in Lösung befindlichen Körper. Nernst: Ztschr. phys. Chem. **2,** 613 (1888).—The amount of a dissolved non-electrolyte S passing through the volume-element qdx of a cylinder will be directly proportional to the cross-section q of the cylinder, to the difference of osmotic pressure dp, and to the time t; but inversely to the distance dx passed through, or $S = -\frac{qt}{K} \cdot \frac{dp}{dx}$; (1), where the proportionality-factor K denotes the force necessary to give one gram-molecule the velocity of one cm. per second; the *minus* sign is due to the fact that the substance diffuses from a place of greater to one of less concentration. If c = concentration and p_0 = osmotic pressure in a solution having the concentration 1, then $p = p_0 c$ and (1) becomes $S = -\frac{qtp_0}{K} \cdot \frac{dc}{dx}$; (2). The author calculated the values of K for various substances from the velocities of diffusion, on the assumption that the formula $pv = RT$ holds good for all pressures.

	Urea.	Chloral Hydrate.	Mannite.	Cane Sugar.
T	280.5	282	283	282
$K.10^{-9}$ kg.	2.5	3.8	5.5	6.7

For completely dissociated, binary electrolytes equation (2) will apply if we add a term due to the fact that the two ions must diffuse equally fast in order to prevent an accumulation of free electricity in the liquid. If J_K and J_a be the value of K for the cation and the anion respectively, and u and v the migrating velocities of the same, the correction for the cation will be $\frac{p_0}{J_K} \cdot \frac{u-v}{u+v} \cdot \frac{dc}{dx}$, and for the anion, $\frac{p_0}{J_a} \cdot \frac{u-v}{u+v} \cdot \frac{dc}{dx}$, whence

$$\left.\begin{aligned} S_K &= -\frac{qtp_0}{J_K}\left(1 - \frac{u-v}{u+v}\right)\frac{dc}{dx} = -\frac{qtp_0}{J_K} \cdot \frac{2v}{u+v} \cdot \frac{dc}{dx} \\ S_a &= -\frac{qtp_0}{J_a}\left(1 - \frac{v-u}{u+v}\right)\frac{dc}{dx} = -\frac{qtp_0}{J_a} \cdot \frac{2u}{u+v} \cdot \frac{dc}{dx} \end{aligned}\right\} \quad (3)$$

Equation (3) can be used to determine S_K and S_a when J_K, J_a, u and v are known. The theoretical results vary from the observed data in few cases by more than 10 per cent.

[1] The present report outlines the main features of the recent work of Nernst, whose papers on Chemical Theory have, for brilliancy and importance, already become classics. Two of them: Ztschr. phys. Chem. **4,** 372 and **9,** 137, have been included in the previous reports.—J. E. T.

When the dissolved substance is a partially dissociated electrolyte we can consider the undissociated salt as diffusing also, and have a combination of equations (2) and (3). The case of the mixture of two salts having a common ion is similar in principle to that of a single salt, except that we have here the condition that the amount of the common ion passing through the volume-element must be equal to the sum of the amounts of the two other ions passing through the same volume in the same time. Although the general idea of this case is simple, the mathematical statement of it presents such difficulties that the author contented himself with approximations, the details of which, together with the paragraph on the change of the coefficient of diffusion with the temperature, cannot be given here. W. D. B.

Die elektromotorische Wirksamkeit der Ionen. Nernst: Ztschr. phys. Chem. **4**, 129 (1889).—If the migrating velocities of the cation and anion be u and v respectively, the work done in carrying the cation from a place of osmotic pressure p_1 to one of p_2 will be $\frac{u}{u+v}\int_{p_1}^{p_2} Vdp$, and to bring the anion from p_2 to p_1, $\frac{v}{u+v}\int_{p_2}^{p_1} Vdp$. Substituting for V from Boyle's Law $pV=p_0$ and integrating, we have for the work, or the electromotive force, the expression

$$E=\frac{u-v}{u+v}\cdot p_0 \log \frac{p_1}{p_2}. \qquad (1)$$

If $u>v$ and $p_1>p_2$, E is positive and the current flows through the cell from the more to the less concentrated solution. The value of the E. M. F. is seen to depend, not on the absolute values of p_1 and p_2, but on their ratio. Substituting for p_0 we have

$$E=\frac{0.860\,T(u-v)}{u+v}\cdot \log \frac{p_1}{p_2}\times 10^{-4} \text{ volts}. \qquad (2)$$

In the following cell p_1 and p_2 denote the osmotic pressures of the ions in the different solutions, u_1, u_2, and v_1, v_2 the migrating velocities of the cations and anions respectively.

$$\text{El.}\,p_1u_1v_1 \overset{1}{|}\, p_2u_1v_1 \overset{2}{|}\, p_2u_2v_2 \overset{3}{|}\, p_1u_2v_2 \overset{4}{|}\, p_1u_1v_1\text{El}.$$

The circuit is closed by like electrodes in the same solution p_1, u_1, v_1; so that no E. M. F. is generated at these contacts. The E. M. F.'s at contacts 2 and 4 are equal and opposite, and we have only to consider those at 1 and 3, which by (2) will be

$$E=0.860\,T\left[\frac{u_1-v_1}{u_1+v_1}-\frac{u_2-v_2}{u_2+v_2}\right]\log\frac{p_1}{p_2}\times 10^{-4}\text{ volts}. \qquad (3)$$

If $\frac{u_1-v_1}{u_1+v_1}>\frac{u_2-v_2}{u_2+v_2}$ and $p_1>p_2$ the current will flow through the cell from the more to the less concentrated solution. This was

confirmed in every case. The calculated E. M. F. was 13 per cent. higher than the observed when salt solutions were used, 6 per cent. for acid solutions. The reason for this variation is not yet known.

If we have an electrode, non-polarizable in regard to the cation —such as a metal in a solution of its own salt—the work necessary to force the amount of the cation bearing the unit quantity of electricity, out of the solution, will be, if p is the osmotic pressure of a univalent cation,

$$dE = -Vdp = -p_0 d\log p,\ E = -p_0 \log p + p_0 \log P = p_0 \log \frac{P}{p},$$

where $p_0 \log P$ is the constant of integration. Substituting for p_0,

$$E = 0.860\, T \log \frac{P}{p} \times 10^{-4} \text{ volts.} \qquad (4)$$

For an electrode, reversible in regard to the anion, such as silver, silver chloride in a chloride solution, we have

$$E = 0.860\, T \log \frac{p}{P} \times 10^{-4} \text{ volts.} \qquad (5)$$

These formulæ were not tested directly, but were developed in order to make the E. M. F. of another form of concentration-cell capable of calculation. For a cell of the type Ag, p_1 $AgNO_3$ | p_2 $AgNO_3$, Ag, we have from (2) and (4),

$$E = 0.860\, T \left[\log \frac{P}{p_1} + \frac{u-v}{u+v} \cdot \log \frac{p_1}{p_2} - \log \frac{P}{p_2} \right] \times 10^{-4} \text{ volts,}$$

$$E = 0.860\, T \cdot \frac{2v}{u+v} \cdot \log \frac{p_2}{p_1} \times 10^{-4} \text{ volts.} \qquad (6)$$

The corresponding formula for a cell non-polarizable in regard to the anion is

$$E = 0.860\, T \cdot \frac{2u}{u+v} \cdot \log \frac{p_1}{p_2} \times 10^{-4} \text{ volts.} \qquad (7)$$

Equation (7) was tested by the author in a large number of cases and the agreement between theory and experiment was very satisfactory.

The author showed further that the (apparently) very different formula of Helmholtz, connecting the E. M. F. of concentration-cells with the vapor-pressures of the solutions, reduces to formula (6) when one substitutes van't Hoff's expression for the change of the vapor-pressure with the concentration.

The term P in formulæ (6) and (7) expresses the tendency of the electrode to go into solution, thus corresponding to the vapor-tension of a liquid. As we must admit the existence of a vapor-tension, though a very small one, for metals, they must have a solution-tension also.[1] The reason given by Helmholtz and

[1] Or Vapor-pressure and Solution-pressure, the terminology adopted elsewhere in these reports.—J. E. T.

Nernst why the metals do not dissolve more is that the metal goes into solution as an ion and, with the enormous electrical charges which the ions are assumed to have, equilibrium takes place before an appreciable quantity has been dissolved. This view offers no explanation for the fact that metallic vapors do not conduct.

The author obtained an expression for the E. M. F. of a concentration-cell where the solutions are at different temperatures, by substituting for p from the van't Hoff expression $p = a\mu T$, where a = constant and μ = concentration in gram-equivalents per liter. In cells with mercury electrodes the current passed through the solutions from the cold to the warm contact. The numerical results obtained between different ranges of temperature were thoroughly discordant.

In closing, the author treated the effects upon the electromotive forces of several of the non-polarizable cells in actual use, due to the changes of concentration in the component solutions. His qualitative conclusions were in all cases in accordance with the facts; quantitative predictions were impossible, the solution tensions of the metals being not yet determined.

This paper is one of the most important in modern physical chemistry and deserves careful study, both for the ideas developed in it and on account of the vast amount of important research which it not only suggests but makes necessary. W. D. B.

Ueber ein neues Prinzip der Molekulargewichtsbestimmung. W. Nernst: Ztschr. phys. Chem. **6**, 16 (1890).—Dissolved substances decrease the vapor-pressures of their solvents;[1] they must also decrease in the same manner the solution-pressures[2] of these solvents as towards a second liquid. In order to derive strictly the relation between solubility and osmotic pressure the author presupposes the equation of condition of dissolved substances, $pv = RT$, and the expression for the work required to compress a dissolved gram-molecule from the volume v_1 to v_2, *i. e.*,

$$\int_{v_2}^{v_1} p\,dv = RT \int_{v_2}^{v_1} \frac{dv}{v} = RT \log \frac{v_1}{v_2} = RT \log \frac{p_2}{p_1}.$$

Suppose in contact two liquids, A and B, very slightly reciprocally soluble, N gram-molecules of A containing in solution n gram-molecules of a substance of osmotic pressure π; suppose also pure solvent A in contact with B. This gives two pairs of liquids: (I) solution in A; (Ia) solution of A, with osmotic pressure p', in B (in equilibrium with I); (II) pure A; (IIa) saturated solution of A, with osmotic pressure p, in B.

Carry a gram-molecule of A in isothermal, reversible cycle from I to Ia where it fills volume v' (work done, $-p'v' = -RT$); from Ia to IIa (work done, $+RT \log \frac{p}{p'}$); from IIa to II (work done,

[1] *Cf.* This Journal **15**, 138. [2] *Ibid.* **15**, 141.

$pv = +RT$); from II to I, S = molecular volume of A, (work done, $-\pi S$). Here Σ work = 0 (2d Law of Thermodynamics), so $\pi S = RT \log \frac{p}{p'}$. Substituting for $\log \frac{p}{p'}$ A's relative solubility-depression $\frac{p-p'}{p}$ and for π and $\frac{V}{S}$ their values $\frac{RT}{V}$ and $\frac{N}{n}$ (V is volume of I per gram-molecule dissolved substance), we have $\frac{p-p'}{p} = \frac{n}{N}$. This is also the equation for van't Hoff's vapor-pressure law of solutions.[1] In words: on adding a foreign substance to a solvent, the relative solubility-depression of the latter towards a second liquid is the ratio of the number of molecules added to the number of those of the solvent.

Dissolving in 100 grams valeric acid g grams of a substance of molecular weight M, $n = \frac{g}{m}$ and $N = \frac{100}{102}$, hence $M = \frac{102g}{100} \cdot \frac{p'}{p-p'}$. The solubility p of valeric acid in water was found by titration, the decrease $p-p'$ by a subsequent titration, after adding to the excess of acid the substance to be studied. The molecular weights thus found by a single titration were, *e. g.*,

	Mol. wt.	Found.
Chloroform	119.5	118
Menthol	156	161
Stearic acid	284	291

Excellent results were obtained also from the depression of the solution-pressures of ether and of ethyl acetate towards water.

Additional data and specific instructions for a practical method for accurate work are given in a later paper.[2] 20 cc. ether (freed from alcohol by shaking out with water and drying over sodium) and 5 cc. water are placed in a Beckmann freezing-apparatus. Add the substance (which must be quite insoluble in water), g grams per 100 grams ether; from the total ether used subtract 0.8 gram, the amount dissolved by the water. The freezing-point rises $t°$ from about $-3.85°$. The corrected rise of freezing-point is $t' = t \cdot \left(1 + \frac{t}{3.85}\right)$, the molecular weight is $M = E \cdot \frac{g}{t'}$. The "molecular rise" E is 3.06. With vigorous super-cooling very accurate readings are obtainable. Results cited are, *e. g.*,

	Mol. wt.	Found.
Benzene	78	78–82
Naphthalene	128	128–131
Carbon bisulphide	76	72–78

Ein osmotischer Versuch. W. Nernst: Ztschr. phys. Chem. **6**, 37 (1890).—That the singular action of semi-permeable mem-

[1] *Cf.* This Journal **15**, 138. [2] Ztschr. phys. Chem. **6**, 573.

branes is accounted for by the solubility law derived in the preceding paper is illustrated by the following experiment: Over an inverted funnel-tube is stretched a porous membrane saturated with water, the funnel containing a solution of benzene in ether, and being submerged in ether. The solution and the pure ether are thus separated by a water-layer, towards which the solution-pressure of the first is diminished by the presence of the benzene, which, being insoluble in water, cannot of itself pass the membrane. The excess of pressure of the pure ether towards the water layer causes it to diffuse through the membrane, diluting the benzene solution and raising its level in the tube until the pressure-difference is counterbalanced by the weight of the column. The ether used is first saturated with water to prevent it dissolving the water-layer. According to this, the activity brought about by the osmotic pressure in plant-cells is due to the solubility of water, and the non-solubility of the dissolved substances of the sap, in protoplasm.

Verteilung eines Stoffes zwischen zwei Lösungsmittel und zwischen Lösungsmittel und Dampfraum. W. Nernst: Ztschr. phys. Chem. **8**, 110 (1891).—In this very important paper Nernst has developed the theory of the vapor-pressures of solutions of volatile substances, and that of the distribution of a dissolved substance between two solvents. From van't Hoff's law, that a substance having the same molecular weight in gas and solution dissolves proportionally to its gas-pressure, he arrives at the Law of Distribution:—*At a given temperature each sort of molecule has a constant ratio of distribution between solvent and vapor, or between two solvents, independent of the presence of other sorts of molecules, and whether reacting chemically with them or not.* Different "sorts of molecules" are not only those of different substances, but also double molecules, single molecules, and different ions. Comparison with known data on the distribution of bromine or iodine between water and carbon bisulphide (Br_2 and I_2 in both solvents) shows a satisfactory agreement. Experiments with salicylic and with benzoic acids shaken with water and benzene—these acids being largely bimolecular in benzene and somewhat dissociated into ions in water—show the *total concentrations* in the two solvents not even approximately proportional, the concentrations of the normal molecules, however, to be entirely so.

When N gram-molecules solvent contain n gram-molecules of a volatile substance whose molecular weight is the same in solution and in vapor, the composition of the vapor of the solution is readily found. Here the partial pressure p of the dissolved substance is proportional to its concentration $\frac{n}{N+n} = kp$, that of the solvent is $P = P_0 \frac{N}{N+n}$, P_0 being its vapor-pressure in pure con-

dition. The molecular concentrations in the vapor are then, of course, given by these values of p and P. The formulæ represent more closely the measurements of Winkelman than does the similar theory of Planck.[1]

The most interesting case is that of a substance having different molecular condition in solution and gas, as acetic acid, which is almost entirely bimolecular in benzene but largely monomolecular as vapor. Setting proportional the concentrations of the normal molecules in both solution and vapor, an expression for p is obtained, which yields results in striking agreement with the values found directly from the boiling-points of the solutions. With barometric pressure $B = 750$, $p = B - P$ and, combining with van't Hoff's vapor-pressure formula, $p = B - P_0 \frac{N}{N+n}$, n dissolved molecules causing ΔT change of boiling-point, P_0 at the actual boiling-temperature becomes $P_0 = B + \frac{dP_0}{dT} \cdot \Delta T$, and so $p = B\left(\frac{n}{N+n} - \frac{dP_0}{dT} \cdot \frac{\Delta T}{B} \cdot \frac{N}{N+n}\right)$. $\frac{dP_0}{dT} = 22.2$ is found from $\frac{dP_0}{dT} = \frac{\rho}{Tv}$ (Clausius), and the gas-equation. Terming C the actual total molecular concentration $\frac{n}{N+n}$, the dissociation being found from the freezing-points, the desired pressure is

$$p = 750C - 22.2\Delta T(1 - C) \text{ mm. mercury.} \qquad (1)$$

From the dissociation-isotherm $\frac{m\alpha}{1-\alpha} = k$ (m and α = percentage concentration and dissociation, respectively), the concentration of the normal molecules in the solution is proportional to $\sqrt{m(1-\alpha)}$. From the density, Δ, of the vapor, and its theoretical density, δ, at dissociation $\alpha' = 0$, results $\alpha' = \frac{\delta - \Delta}{\Delta}$, and the concentration of the normal molecules in the vapor is $p\Delta \cdot \frac{\delta - \Delta}{\Delta} = p(\delta - \Delta)$. The Law of Distribution requires $14.4\sqrt{m(1-\alpha)} = p(\delta - \Delta)$, or

$$p = 14.4 \frac{\sqrt{m(1-\alpha)}}{\delta - \Delta} \text{ mm. mercury,} \qquad (2)$$

the proportionality-factor, the inverse solubility-coefficient of the normal molecules, being 14.4. A few of the results, giving the partial pressures of the acid-vapor, as directly found from (1), and as found from the Law of Distribution from (2), are:

Grams acid.	α.	p from (1).	p from (2).	Δ.	α'.
0.663	0.10	6.6	6.5	2.44	0.70
5.00	0.038	23.6	23.9	2.83	0.47
8.42	0 029	36.4	36.5	3.02	0.36

[1] Ztschr. phys. Chem. **2**, 405.

This agreement is one of the most brilliant achievements of the modern Physical Chemistry. Similar experiments with solutions of water in ether led to the result that, of the $(H_2O)_2$ molecules present in a 1.315-per cent. solution, about 58 per cent. are dissociated into the simple molecules H_2O. In connection herewith Walker's conclusion, that water in ether is *almost entirely* bimolecular,[1] is shown to be incorrect, his formulæ requiring the solubility of pure water, not of water saturated with ether, in ether.

Qualitative application of the theory shows that, for example, the partial pressure of hydrochloric acid over its aqueous solution increases, if an electrolyte with a common ion be added; decreases, if the second electrolyte have not a common ion; that in concentrated solution salicylic acid will be in great measure taken up by benzene, if dilute will go into the water-layer, but can be driven into the benzene by adding a strong acid or a salicylate. Further applications suggest themselves.

Ueber die Maximaltension, mit welcher Wasserstoff aus Lösungen durch Metalle in Freiheit gesetzt wird. G. Tammann und W. Nernst: Ztschr. phys. Chem. **9**, 1 (1892).—A metal acting upon aqueous acids liberates hydrogen, whose partial pressure when in equilibrium with metal and solution is termed its "maximum pressure" p. The work gained in liberating 2 grams hydrogen, transferred to pressure P, is $W = pv + RT \log \frac{p}{P}$. The work gained in a Daniell's cell in dissolving 1 gram-molecule of zinc and precipitating 1 gram-molecule of copper is then $W_1 - W_2 = RT \log \frac{p_1}{p_2}$, which is equal to the E. M. F. E; or

$$E = 0.430\, T \times 10^{-4} \log \frac{p_1}{p_2} \text{ volts.}$$

This relation renders possible for the first time a calculation of the E. M. F. of a reversible element from accessible, extraneous data. Combination with the Clausius vaporization-formula yields the famous equation of Helmholtz, $W - E = -T \cdot \frac{dE}{dT}$.

According to Nernst's electrolytic solution-pressure theory, a metal drives another out of solution by reason of its superior solution-pressure, and a metal liberates hydrogen with acids only when the pressure of the gas over its solid solution in the metal exceeds one atmosphere.

In the experimental work of the authors, metal and acid were brought together in sealed tubes, the pressure of the freed hydrogen being measured manometrically. Their apparatus usually exploded at pressures approximating 70–90 atmospheres, proving the electrolytic solution-pressures of the metals to be great.

[1] *Cf.* This Journal **15**, 143.

Successful experiments with dilute acids showed the pressure rapidly to increase with the acid-concentration and to be strongly depressed by the presence of neutral salt.

Osmotischer Druck in Gemischen zweier Lösungsmittel. W. Nernst: Ztschr. phys. Chem. **11**, 1 (1893).—If a mixture of solvents contain in volume v 1 gram-molecule of dissolved substance of osmotic pressure π, removal of v therefrom requires work πv. This can be accomplished by isothermal vaporization. Suppose v composed of n_1 and n_2 gram-molecules of each component, respectively: their partial pressures over pure mixture and solution being p_1, p_1' and p_2, p_2' respectively. Transferring the n_1 gram-molecules from solution to pure mixture requires work $n_1 R T \log \frac{p_1}{p_1'}$; transferring both n_1 and n_2 requires then

$$\pi v = n_1 R T \log \frac{p_1}{p_1'} + n_2 R T \log \frac{p_2}{p_2'} = R T; \text{ or } n_1 \log \frac{p_1}{p_1'} + n_2 \log \frac{p_2}{p_2'} = 1.$$

It is proposed to determine the pressures entering into this equation, from the boiling-point changes of the solutions and the composition of their vapors. Accounting for the variation of pressure with temperature, by application of the Clausius vaporization-formula $\frac{dp}{dT} = \frac{\rho}{Tv}$, and making the necessary reductions, there results

$$\frac{1}{E} = \frac{1}{E_1} \cdot \frac{q}{100} + \frac{1}{E_2} \cdot \frac{100 - q}{100}.$$

E, E_1 and E_2 represent the molecular rise of boiling-point for the mixture and for each component, the mixture consisting of q grams of one, per 100 grams of both, *i. e.*, the molecular rise of boiling-point is simply additive.

Studien über die Verwendbarkeit des Beckmannschen Siedeapparates. Max Roloff: Ztschr. phys. Chem. **11**, 7 (1893).—Careful determinations of the boiling-points of aqueous solutions of potassium chloride are compared with the vapor-pressures of water at the same temperatures, to obtain the relative depressions. The osmotic pressures are calculated therefrom according to the ordinary van't Hoff formula: $\pi = R T \cdot \frac{s}{M} \cdot \log \frac{p_1}{p}$. M is the molecular weight of potassium chloride; s the specific gravity of the solution. Tabulated values from 3.23 to 112.3 atmospheres and the corresponding ΔT's are given.

With the boiling-point method are obtained the individual partial pressures in the vapors of aqueous solutions of formic, acetic, hydrochloric and nitric acids of varying concentrations. The theory is that of Nernst, as reviewed above.

Nernst's theory of the osmotic pressures of solutions in mixed solvents is tested in the manner indicated in the preceding review.

Solutions of naphthalene in benzene and chloroform and of boric acid or potassium chloride in water and acetic acid are studied, and a brilliant agreement with the theory demonstrated.

The Beckmann boiling-point apparatus is adapted to determinations under varying pressures by connection with an air-pump and an oil manometer. The method shows a surprising accuracy and is applied in determining the change of boiling-point of water with the temperature. Figures agreeing with the famous determinations of Regnault are readily obtained. Extensive application is prophesied for the new method.

Ueber die Farbe der Ionen. W. Ostwald: Ztschr. phys. Chem. **9**, 579 (1892).—Experience regarding absorption-phenomena of undissociated compounds in solution shows substitution in the molecule to effect distinct alteration in the light-absorption and color. In a salt-solution of finite concentration, the absorption-spectrum of the electrically neutral molecules present, together with that of each of the ions, constitutes that of the solution. At high dilutions, where the dissociation is quite complete, all salts with the same colored ion must have the same absorption-spectrum and color, if the other ion be colorless. To establish this conclusion, as against the statements of Krüss[1] and Knoblauch,[2] the author both measured and photographed the absorption-spectra of about 300 salts, including, *e. g.*, 17 salts of diazo-resorcin and 20 of para-rosaniline. The published measurements and heliotype prints conclusively show the spectra of dilute solutions of different salts with the same colored ion, to be identical. Ewan has reached the same result for solutions of copper salts.[3]

Ueber Azofarbenspektra. C. Grebe: Ztschr. phys. Chem. **10**, 673 (1892).—References to the recent literature showing changes in the molecule to condition corresponding changes in the absorption-spectrum are given by Vogel[4] and Schütze.[5] Vogel emphasizes the influence of the *position* of the substituents, Schütze the relation between constitution and color. To obtain extended and comparable results Grebe studies the relation between the constitution and absorption-spectra of over one hundred azo-dyestuffs in solution in concentrated sulphuric acid. Curves representing the intensity of the absorption accompany the paper. With increasing number of carbon atoms the absorption-bands moved without exception from violet towards the red. Substituting hydroxyl or the amido group produces the same effect. The opposite effect is produced by the sulpho group, the numerical value of the change being always practically the same. The position of the substituents has an entirely regular influence.

[1] Ztschr. phys. Chem. **2**, 390 (1888).
[2] Ann. der Phys. Wied. **43**, 767 (1891).
[3] Ewan: Phil. Mag. **33**, 317 (1892).
[4] Ann. der Phys. Wied. **43**, 449.
[5] Ztschr. phys. Chem, **9**, 109.

Methyl- und Ethylalkohol als Lösungsmittel. C. A. Lobry de Bruyn: Ztschr. phys. Chem. **10**, 782 (1892).—Determinations of the solubilities of about forty anhydrous substances, mostly salts, at 15°–25°, confirmed the rule of Dumas and Péligot that in solvent power methyl alcohol stands between ethyl alcohol and water. Hydrochloric acid, mercuric chloride and iodide and the aromatic nitro compounds form exceptions. Methyl alcohol replaces the two molecules of water of crystallization in copper chloride, barium bromide, mercuric chloride, and cobalt sulphate; ethyl alcohol, however, does not. The sulphates with water of crystallization dissolve in methyl alcohol to as much as 60 per cent., but these concentrated solutions are mostly unstable, those of zinc, copper, cobalt, and magnesium precipitating crystals in a few minutes, others, as of nickel and iron, after days or weeks. This almost entirely decolorizes the solutions of salts of nickel, copper and cobalt. The salt $NiSO_4.6H_2O$ remains in solution. A few drops of water, or a temperature-rise, greatly accelerates the precipitation in all cases. The solution of the salt $MgSO_4.7H_2O$ clouds on heating, but clears again on cooling. The precipitates are, in some cases, crystals with less water; in others the water is partially replaced by alcohol. Similar phenomena with ethyl alcohol are less striking, since it dissolves the salts to only 1 or 2 per cent. The author suggests that these hydrates may exist as such in solution in methyl alcohol.

Ueber Oxydationsketten. W. D. Bancroft: Ztschr. phys. Chem. **10**, 387 (1892).—By means of a galvanometer the author measured the E. M. F. of systems composed each of an oxidizing and a reducing agent separated by an indifferent salt solution or by mercury. The E. M. F. of the cells was found to be, within the experimental error of about ±0.02 volts, independent of the nature of this connection, as well as of that of the electrodes, which were for the most part of platinum. It was shown further to be additive, being the sum of the potential differences of electrode and solution; extended tables of these experimentally determined differences are given. It was found also to remain constant for a wide range of concentrations. The nature of the indifferent (not oxidizing or reducing) ion exerts no effect upon the E. M. F., except that a free acid is a stronger oxidizing agent than is the corresponding salt, the contrary holding for reducing agents.

TREVOR.

CORNELL UNIVERSITY.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. By ARTHUR H. ELLIOTT, Ph. D., Professor of Chemistry and Physics and Director of the Chemical Laboratory in the College of Pharmacy of the City of New York. Published by the Author.

Books for laboratory instruction in qualitative analysis are so numerous that they can vary but little. In Prof. Elliott's book

the list of the commercial compounds of each metal is of value to the student. The special tests for the single metals are well chosen; the directions for separating the metals are very clear and contain many minor details indispensable to the operations, but usually omitted from books of this kind. Herein lies the value of the book, which can be recommended as an excellent manual. While commending the book, one may differ from the author as regards methods of laboratory instruction. To quote from the introduction: "Above all things the student should work with the instructor, and at exactly the same moment, upon the same materials and with a parallel set of apparatus, thus insuring success and giving a confidence inspired by no other method of working. The method here described can be readily applied in classes of one hundred if the instructor is on a raised rostrum where he can be easily seen by every member of the class." If an instructor has to struggle single-handed with a class of a hundred students this method is, doubtless, the best under the circumstances, but then it is the circumstances which are wrong. Surely in the laboratory each student should work independently, neither held back nor dragged on by others. The instructor should study each individual student and demand work from him in proportion to his ability. Where each instructor has not more than fifteen or twenty students to care for on a given day this is possible; with limited time and unwieldy classes it is not, and then the "test-tube drill" and similar devices for mass-instruction come into play. E. R.

NOTES.

A New Electric Furnace.

Henri Moissan describes[1] a furnace in which the heat of the electric arc is utilized. The furnace is a chamber of carbon having the form of an upright cylinder, standing on a carbon plate, and covered with a carbon disk. The cylinder is placed in a block of quicklime, an air space of 5 mm. being left between the cylinder and the lime. The dimensions of a furnace for a current of 300 to 500 ampères are 6 cm. in height, 5 cm. in diameter. The horizontal carbon electrodes are 3 cm. in diameter, and pass through circular openings cut in the cylinder and in the block of lime; they are so mounted that the distance between their points can be regulated. The current is furnished by a dynamo.

Moissan says that the only limit to the obtainable temperature is that of the electric arc, and that temperatures above 3000° are readily obtained. E. R.

[1] Compt. rend. **116**, No. 3.

Studies on the Properties of Carbon, and the Preparation of Diamond.[1]

Henri Moissan describes in No. 7, the analysis of a meteorite found in the Cañon Diablo in Arizona, and presented to the French Academy. One fragment had on its surface a point of great hardness, which scratched steel, and was surrounded by carbon and iron carbide. Moissan treated the fragment by Berthelot's methods, to remove foreign matter and separate from each other different forms of carbon. Berthelot has shown that a mixture of nitric acid and potassium chlorate oxidizes amorphous carbon completely to carbon dioxide, graphites to graphitic acid, or graphitic oxides, and does not attack diamond. The fragment was treated with boiling hydrochloric acid till all iron was dissolved. The residue contained (1) a fine powder of carbon, perhaps resulting from the decomposition of iron carbide; (2) carbon in minute fragments, brown in color, resembling the carbon found in suddenly-cooled cast iron; (3) a carbon of high density in rounded fragments mixed with iron phosphide and metallic nickel. After treatment with boiling sulphuric acid and with hydrofluoric acid alternately (which removed everything excepting carbon), the density of the residue was found greater than that of methylene iodide. It was then treated eight successive times with a mixture of boiling nitric acid and potassium chlorate. There remained two minute yellow diamonds of specific gravity much greater than methylene iodide, scratching ruby, burning in oxygen to carbon dioxide. The largest diamond measured 0.7 by 0.3 mm.

In another fragment of the meteorite, black diamond, the so-called carbonado, was found. This is the first time that diamond has been found in meteorites.

In the same number of the *Comptes Rendus* is another article by Moissan, giving the analyses of the "blue earth" of the South African diamond-fields. This is a serpentine breccia in which the diamonds are found. Analysis shows that this blue earth contains microscopic transparent diamonds, carbonado or black diamond, and crystallized graphite.

In No. 6 Moissan describes the preparation of diamond by the crystallization of carbon at high temperature and high pressure. His method of work is ingenious. The temperature required was easily reached in the electric furnace described above. To obtain a high pressure at high temperatures, he utilized the increase in volume of fused iron passing from the liquid to the solid condition: iron, like water, expands at the moment of taking the solid form. Pure carbon, prepared from sugar, was tightly compressed into a small wrought-iron cylinder closed by a cap screwed on.

200 grams of wrought iron were melted in a carbon crucible in the electric furnace—an operation requiring only a few

[1] Compt. rend. **116**, Nos. 6, 7, 10, 12.

moments—and the cylinder containing the carbon was then plunged into and completely immersed in the molten iron. The crucible was then lifted from the furnace and placed in a vessel of water, causing the quick formation of an outer layer of solid iron; when this crust had cooled to a dark-red heat, the crucible was taken from the water and allowed to cool in the air.

On treating the metallic mass with boiling hydrochloric acid until all iron was dissolved, there remained three varieties of carbon: graphite, amorphous brown carbon, and carbon of high specific gravity. When this last was treated by Berthelot's method, as described above, there remained minute diamonds, some black and some transparent, but showing all the properties of diamond.

Moissan varied the experiments: In one series, fused iron saturated with carbon at 2000° was cooled in a current of illuminating gas. This experiment yielded microscopic transparent diamonds resembling those found in the blue earth of the diamond-fields. In another series of experiments silver was substituted for iron, as silver has the same property of expansion on passing from the liquid to the solid state. This series of experiments was very interesting. Of course the temperature required was lower than with iron, and no transparent diamonds were obtained, but an abundance of carbonado; specimens of this from different experiments showed different densities—from 2.5, the density of graphite, to 3.5—thus showing an increasing hardness from amorphous carbon, through the soft and hard graphites and colored diamonds of increasing density, to the transparent diamond. The carbonado of density 3.5 scratches ruby.

Moissan concludes by saying that though he made many trials with the fused iron, in only a few experiments has he succeeded in obtaining transparent diamonds, and then only in minute quantities.

In No. 10, Moissan has an article on the analysis of the ash of the impure diamond, which always contains iron and silicon, and, often, lime.

In No. 12 is an article on a variety of graphite which puffs up when heated on platinum foil, after treatment with nitric acid, behaving somewhat like mercuric sulphocyanide when heated. Prof. Luzi first called attention to this phenomenon,[1] and shows that some natural graphites behave thus, while others do not. Luzi calls the first variety graphites; the second, graphitites.

Moissan finds that when molten cast iron is suddenly cooled with water, ordinary graphite is formed on the surface, and below the surface another variety of graphite giving Luzi's reaction. To obtain this last variety alone it is better to employ platinum instead of iron. He fuses in the electric furnace 200 grams of platinum in a carbon crucible. The platinum melts rapidly and after a few minutes distils from the crucible as a vapor, condensing in drops

[1] Ber. d. chem. Ges. **25**, 214.

of molten metal on the cooler parts of the electrodes. The liquid platinum becomes rapidly saturated with carbon at this high temperature, part forming a carbide of platinum. On cooling the excess of carbon is found in the form of crystals of graphite scattered throughout the mass. This graphite shows Luzi's reaction.

Moissan has examined the products of this reaction. He finds that oxides of nitrogen and a little carbon dioxide are given off; the swelling up of the graphite on heating is caused by the escape of these gases. The formation of these gases may be due to the presence of small quantities of amorphous carbon between the crystal surfaces of the graphite, or perhaps to the decomposition by heat of a little graphitic oxide, formed by nitric acid attacking the softer particles of graphite. E. R.

Notes on the Rapid Preparation of Refractory Metals at High Temperature.[1]

Moissan has used his electric furnace to prepare uranium, manganese, chromium, cobalt and nickel, by reduction of the oxides of the metals in carbon crucibles. The action is similar to that of a blast furnace, inasmuch as the products are not pure metals, but are carbides of the metals. The proportion of carbon varies in the products of different experiments:

	Percentage of Carbon.
Uranium carbide	5—13.5
Manganese "	6—14.5
Nickel "	6—13.5
Cobalt "	7— ...
Chromium "	8—12

The only products are carbon and the desired metal: there are no impurities present. The yield is very satisfactory: an ingot of uranium carbide weighing 200–220 grams, was made in ten minutes, with the aid of a current of 450 ampères and 60 volts. The carbide of manganese was prepared in five minutes, with a current of 300 ampères and 60 volts. Chromium carbide was prepared in eight minutes, with a current of 350 ampères and 50 volts.

The reductions can also be made with much weaker currents, requiring more time.

Moissan promises soon to publish methods for obtaining perfectly pure uranium, and manganese from the carbides. To prepare pure chromium from chromium carbide, he breaks the mass into small fragments and brings it into a carbon crucible which has been thickly lined with chromium oxide. The mass is covered with chromium oxide and again heated in the electric furnace. The oxide and carbide are fused, the oxide extracting the carbon

[1] Compt. rend. **116**, No. 8.

from the carbide, which is gradually decarbonized until pure chromium, without a trace of carbon, is obtained. This chromium, heated in a current of dry chlorine, is changed quantitatively into volatile chromium chloride without leaving any trace of residue.

E. R.

Commercial Preparation of the Peroxides of the Alkali Metals.

A method for the preparation of the peroxides of the alkali metals has recently been described,[1] which has as its essential features (1) the use of aluminium for the crucibles to contain the alkali to be oxidized, and (2) the employment for the oxidation of a mixture of oxygen and nitrogen in which the proportion of the latter gas is continually lessened as the process is continued. The temperature is maintained at about 300°.

The alkali is placed in small quantities in trays of aluminium, the latter being arranged on wheels to assist in their introduction into and withdrawal from the furnace. The use of aluminium does away with the difficulties hitherto experienced where trays of other material (as, for example, glass) being employed, a satisfactory product could not be obtained owing to the corrosion of the material of the tray. The aluminium is entirely uninfluenced by contact with the alkali. The trays are run into a closed retort of iron into which a regulated current of air can be made to pass. The air is, of course, completely freed from moisture and carbon dioxide, and, before entering the retort, is mixed with oxygen or nitrogen as may be desired. By the method of employing at first air poor in oxygen and then gradually increasing the proportion of that gas as the area of oxidizing material increases, a slow and uniform action is brought about, and, as a result, a product of practically constant composition.

The process is patented by the (Castner) Aluminium Company, Limited, of London.

W. W. R.

ERRATA IN THE ARTICLE ON REDUCTION OF NITRIC ACID BY COPPER, BY PAUL C. FREER AND GEO. O. HIGLEY.

Page 71, fourth line from the bottom, nitrogen dioxide should read nitric oxide. *Ibid.*, last line, $-12°$ should read 12°.

Page 72, first and second lines, acid represented by the formula $H_2SO_4 + 9H_2O$ should read, sulphuric acid diluted with water, 1:9. *Ibid.*, fourth line, freezing mixture should read cold water.

Page 71, Reference 2 should read [3] **7**, 38.

Page 72, Reference 2 should read **28**, 828.

[1] Monit. Sc. Quesneville [4] **6**, 869.